DOI 10.5162/SMSI2020/P1.9

Resonant Sensor for In-Situ Gas Detection in Heat Treatment Processes

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Summary:
A gas sensor for monitoring of the furnace atmosphere in the production of titanium and carbon based components is tested. The gas sensor is based on *y*-cut $Ca_3TaGaSi_2O_{14}$ (CTGS) piezoelectric single crystal substrates and thin metal oxide sensor films. TiO_2 and $Pr_{0.2}Ce_{0.8}O_2$ sensor films are used for the detection of hydrocarbons, which are formed during the heat treatment of the components mentioned above. The concentration of hydrocarbons provides feedback on the progress of the processes. The successful operation of the gas sensor at temperatures up to 800 °C and in reducing atmospheres is shown.

Keywords: Gas sensor, high-temperature, bulk acoustic wave, thin-films, metal oxides

Background, Motivation and Objective

Manufacturing of high performance materials like titanium or carbon often requires the use of organic additives during shape forming process. Afterwards, these organic additives must to be removed (debinding), which requires high temperatures and is, therefore, energy consuming. Monitoring of decomposition products during heat treatment enables an energy-saving production due to tailored temperature adjustment. For example, the start temperature of decomposition and complete debinding can be identified. Furthermore, the product quality will improve due to more careful heat treatment [1].

The debinding is performed in inert gas atmospheres or in vacuum. Therefore, a high-temperature stable gas sensor withstanding reducing atmospheres is needed. At laboratory-scale, IR spectrometers can be used for selective detection of debinding products. Nevertheless, optical measurement techniques shall not be used routinely in industrial environments due to the required optical path and high costs.

Description of the New System

The gas sensor evaluates changes in sensor film properties, e.g. mass and conductivity, for different metal oxides. It is based on *y*-cut CTGS single crystals which are operated in thickness shear mode by applying an ac voltage via screen printed keyhole shaped platinum electrodes. The metal oxide thin films are deposited on top of the electrodes via pulsed laser deposition. The presence of reducing gas atmospheres affects the conductivity and density of these metal oxides by adsorption/desorption of gas molecules or stoichiometry changes due to e.g. formation of oxygen vacancies. The density change is determined by operating 5 MHz CTGS single crystals as gravimetric sensors, having a mass sensitivity of about 35 cm^2 Hz μg^{-1} even at 800 °C [2]. In addition, a modified electrode layout of such resonators enables to monitor the sensor film conductivity, thereby improving gas selectivity. The related electrode and sensor film layout are shown in Fig. 1.

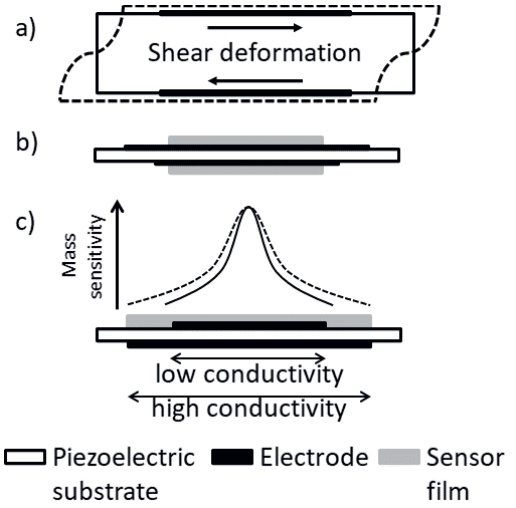

Fig. 1. Piezoelectrically excited resonator with sensor film. (a) Shear deformation, (b) microbalance mode and (c) conductivity mode.

In conductivity mode, a change in sensor film conductivity increases/lowers the excited resonator area, e.g. an increased film conductivity, increases the excited resonator area and, consequently, decreases the resonance frequency. As a consequence, the mass sensitivity and, thereby, the resonance frequency f_R change due to modification of the Gaussian like mass sensitivity distribution and of the piezoelectric stiffened shear modulus [3]. Resonance frequency shifts Δf_R of resonators operated in microbalance mode are a result of mass uptake or loss [4] due to surface adsorption/desorption processes or release/ incorporation of oxygen in the metal oxide.

Results

TiO_2 and $Pr_{0.2}Ce_{0.8}O_2$ sensor films operated in conductivity and microbalance mode are used to investigate the debinding of carbon and titanium based materials (see Fig. 2 and Fig. 3.). The response of the sensor films is measured

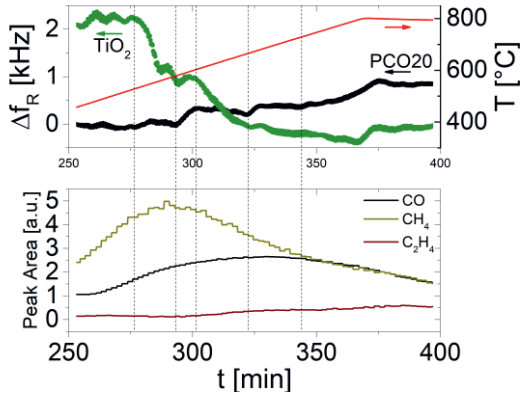

Fig. 2. Shift of resonance frequency Δf_R of resonator coated with TiO_2 and $Pr_{0.2}Ce_{0.8}O_2$ sensor films operated in conductivity and microbalance mode, respectively, for debinding of a carbon based material. In addition, changes in gas concentration are observed using an IR spectrometer.

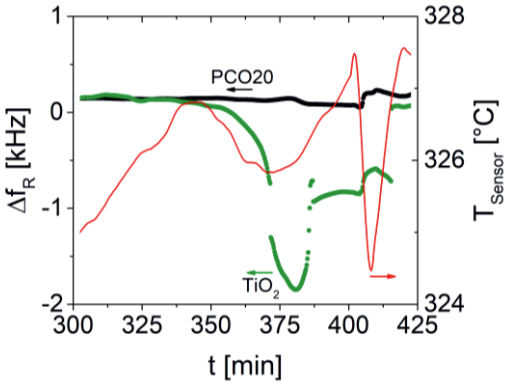

Fig. 3. Shift of resonance frequency Δf_R of resonator coated with TiO_2 and $Pr_{0.2}Ce_{0.8}O_2$ sensor films operated in conductivity and microbalance mode, respectively. The debinding of a titanium based material is observed in an industrial furnace.

throughout the heat treatment, but for clarity only debinding periods are shown.

In laboratory experiments, changes in gas concentration are additionally acquired using an IR spectrometer to evaluate the response of the sensor films. Fig. 2 shows the debinding of an carbon based material at a constant heating rate of 3 K min^{-1} in nitrogen atmosphere. Decrease and increase of f_R are observed for resonators operated in conductivity and microbalance mode, respectively. These responses are expected due to the increase of conductivity for TiO_2 sensor films and mass loss (oxygen) for $Pr_{0.2}Ce_{0.8}O_2$ sensor film. Shifts in resonance frequency Δf_R are a result of increasing methane, ethane and carbon monoxide concentration, because they decrease the oxygen partial pressure of the furnace atmosphere. Fig. 3 shows the debinding of a titanium based material in argon atmosphere and in vacuum of ca. 50 mbar. The sensor films are located in exhaust line of the furnace, which is heated to 200 °C. Here, the response of the TiO_2 sensor film is of special interest. At ca. 335 min, when the furnace reaches 382 °C, the resonance frequency starts shifting as a result of increasing formation of reaction products which affect the conductivity of TiO_2. A maximum frequency shift Δf_R is observed at about 380 min. After about 415 min, when the furnace reaches 485 °C, Δf_R approaches the base level again. The frequency shift indicates the gas formation and marks presumably the start and completion of the debinding.

In order to improve sensitivity and selectivity of the gas sensor, resonator parameters like thickness and electrode/film diameter as well as senor film parameters like film thickness and mass can be tuned.

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