HIGH-TEMPERATURE HYDROCARBON GAS SENSING WITH MESOPOROUS SiO₂ THIN FILMS ON TSM RESONATORS*

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ABSTRACT

A new type of sensor has been developed for the detection of hydrocarbon gases at high temperatures. The sensor consists of a thickness shear mode (TSM) quartz resonator coated with a thin mesoporous silica layer ion-exchanged with palladium ions. When operated at temperatures above 300 °C, the high surface area film catalyzes the combustion of hydrocarbon vapors in the presence of oxygen. The sensor acts as a calorimeter as the exothermic reaction slightly increases the temperature, stressing the sensor surface and producing a measurable deviation in the resonator frequency. Sensitivities as high as 0.44 (ppm-Δf)/(ppm-gas) have been measured for propylene gas, with minimum detectable levels of < 50 ppm of propylene at 500 °C. One potential sensor application is on-line monitoring in vehicle exhaust streams for catalytic converter efficiency or regulatory compliance.

INTRODUCTION

In recent years, acoustic wave devices with specific surface affinity layers have been developed for gas phase chemical sensing [1]. Most of their applicability has been in low-temperature sensing due to the large temperature coefficients of the piezoelectric crystals and limited access to coating materials for high-temperature use. Only a few attempts have been made to adapt acoustic wave sensors to the high temperature region [2,3]. In this paper, we describe a new acoustic wave-based sensing device for high-temperature detection of gaseous hydrocarbons. Many of the previous limitations to high-temperature operation have been overcome or harnessed for specific applications.

A hydrocarbon gas sensor has potential application as an exhaust monitor for internal-combustion (IC) engine vehicles. Residual hydrocarbons, along with nitrogen oxides (NO_x) and carbon monoxide (CO), are present in the vehicle exhaust stream as a result of incomplete fuel combustion. Specifications for on-board hydrocarbon sensors require a measurement range from 25 ppm to 1000 ppm (0.1%) with a detection resolution of 25 ppm. The new acoustic sensor described in this paper shows a capacity to meet these requirements.

The sensor utilizes AT-cut quartz resonators operating in the thickness shear mode (TSM) and coated with a thin layer of surfactant-templated periodic mesoporous silica [4,5] ion-exchanged with metals. AT-cut resonators are commonly used as mass deposition monitors [6] and usually are operated near room

ambient where the resonant frequency deviates little with temperature fluctuations. At much higher temperatures, the frequency response exhibits a nonlinear temperature dependence (see Fig. 1) [7]. Coefficients are > 100 (ppm Δf)/°C above 385 °C and have approximately a quadratic variation with temperature. As seen in Fig. 1, the presence of the thin films has no significant effect on the frequency-temperature curve. The large temperature dependence along with the strain sensitivity of the quartz resonator sensors make them useful for detecting exothermic or endothermic gas reactions as long as the operating temperature is stable and does not exceed the quartz Curie point (α to β phase transition) of 573 °C. At even higher temperatures, other piezoelectric materials such as lithium niobate (LiNbO₃) or gallium orthophosphate (GaPO₄) [8] could be used in a similar fashion since they maintain their piezoelectric properties.

MESOPOROUS SILICA THIN FILMS

Sensitivity and selectivity of chemical sensors is determined by the properties of thin film surface layers. The high-temperature hydrocarbon sensor utilizes a sol-gel deposited surfactant-templated SiO₂ film. An alcoholic acid catalyzed silica sol is prepared with a pH near the isoelectric point of silica [5]. Cetyltrimethylammonium bromide (CTAB) surfactant is added to the sol in concentrations of 1.5 to 4.2 % by weight. After proper masking of the quartz resonator electrodes, the sol is spin-deposited on one surface. The films are then calcined at 400 °C for one hour (using a 1 °C/min ramp up and down) to burn out the organic template and access the porosity. Calcined films resemble

Figure 1. Measured frequency shift vs. temperature for a bare and an SiO₂-coated TSM resonator. Temperature coefficients exceed 100 ppm/°C above 385 °C, but thermal noise reduction is possible using reference sensors and frequency mixing.

* This work was performed at Sandia National Laboratories supported by the United States Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

Figure 2. A TEM image of the [100]-zone of a calcined fragment from a surfactant-templated mesoporous thin film. In this image, the pores have a diameter of ~ 3 nm and a spacing of ~ 8 nm. Choice of surfactant type and concentration determines pore modality and size. Typical film thicknesses are 150 to 200 nm.

the structure shown in Fig. 2. Films prepared using this technique have extremely high surface area (> 700 m²/g), tunable pore diameters between ~ 2.0 and 3.5 nm, and 40-50% porosity. Spin-deposition is controlled to give film thicknesses between 150 to 200 nm. These thicknesses represent a good compromise between needed detection sensitivity and minimal loading and surface stress on the quartz resonator (see Fig. 1).

Gas selectivity is improved by ion-exchanging transition metals into the SiO₂ matrix to catalyze specific interactions. Sensors were prepared with Cu, Pd, Fe, V, Mo, and Cr ions by submersion in low-molarity metal-salt solutions for 5 to 30 minutes. Electron paramagnetic resonance (EPR) spectroscopy was performed on one of the Cu:SiO₂ devices which revealed a density of Cu²⁺ sites of approximately 0.1 atom percent. After a 400 °C anneal, the ion density was slightly reduced. None of the other ion-exchanged sensors were characterized for ion density, however, they are expected to be on the same order as the Cu:SiO₂ device. Full optimization of the ion-exchange process for selective detection is now being performed.

EXPERIMENTAL CONFIGURATIONS

High-temperature evaluations of the metal:SiO₂-coated resonator sensors were performed in a specially-designed test cell. A photo of this test cell is shown in Fig. 3. The cell uses resistance heaters embedded in a metal housing above and below a flow cavity to control temperature. Maximum test temperatures were 500 °C with a control stability of ± 0.1 °C. The resonators are wire-bonded to gold-plated alumina substrates which are configured as RF striplines for carrying electrical signals to the devices. The heated structure around the resonators forms a gas cavity of ~ 2.4 ml volume; an 8 cm long serpentine channel in the test cell cover preheats the gas before introduction into the cavity.

A vapor flow system provided the appropriate mixtures and flow rates for the target gases. Multi-component mixtures (up to three gases) along with a diluent and purge stream (nitrogen or air) were delivered by an array of mass-flow controllers and valves. Source gases were provided from calibrated bottles with desired concentrations or controlled flow through a bubbler (only water was mixed from a bubbler). Gas mixture concentrations using the flow system ranged from 10 ppm to 100%, while flow rates were controlled over the range 0.005 to 0.3 liters/min.

The quartz resonator sensors were configured as part of the Sandia-patented "lever" oscillator circuits that provide two signal outputs: the device resonance frequency (approximately 6 MHz)

Figure 3. Interior view of the high-temperature test cell used for gas exposure of the mesoporous SiO₂-coated resonators. Two TSM resonators — one coated device, one uncoated reference device — are wire-bonded to ceramic striplines. Resistance heater control to 500 °C with ± 0.1 °C stability is possible using the fixture.

and a voltage proportional to the resonant resistance (related to the device quality factor or Q) [9]. Two resonators were mounted in the test cell: one coated device acting as the sensor, and an uncoated device acting as the reference. The frequency outputs from the two devices were mixed, providing a low frequency for measurement and a noise-rejection mechanism for operating in the difficult high-temperature environment (see difference frequency in Fig. 1).

A Windows-based computing system running code written in HPVVEE and Visual Basic handled all sensor data acquisition, test cell temperature control, and vapor flow system control.

RESULTS AND DISCUSSIONS

Several resonators coated with metal ion-exchanged, mesoporous SiO₂ thin films were evaluated for response to hydrocarbon vapors and cross-sensitivity to other gases present in the vehicle exhaust stream. To date, only one type of sensor — a resonator coated with a Pd:SiO₂ film — has shown good sensitivity for hydrocarbon detection. Figure 4 shows the measured frequency shift (in ppm) when this sensor is exposed to repeated intervals of 1 % by volume propylene gas in an oxygen-

Figure 4. Measured frequency shift vs. time for one Pd:SiO₂-coated TSM resonator when exposed to repeated intervals of 1% propylene gas mixed with 20 % oxygen.

Figure 5. Measured frequency shift vs. time for a Pd:SiO₂-coated sensor when exposed to low concentrations of propylene in an oxygen-rich atmosphere. Signal detection is possible below 50 ppm. Negative frequency shifts are seen in this figure (compared to Fig. 4) due to frequency mixing with a reference device.

rich atmosphere at 490 °C. (Propylene gas is used as one simulant for hydrocarbons in vehicle exhaust since it exists in a higher concentration than other non-methane organic gases and has one of the highest reactivity factors.) Maximum sensitivity at 490 °C to propylene vapors is ~ 0.44 (ppm-Δf)/(ppm-gas). Sensor response is rapid, < 20 sec., however, full evaluations of this feature were limited by the 10 sec. data acquisition interval of the measurement system. The minimum detection capability for the Pd:SiO₂ sensor is < 50 ppm propylene at 500 °C as shown in Fig. 5. Smaller propylene concentrations produce noticeable deviations in the frequency response, but it is not certain what fraction of this response is thermal noise created by slight flow rate changes as the vapor delivery system toggles between the target and purge gases.

This sensor functions much like a typical calorimeter or combustible gas detector [10-12]. Figure 6 shows that measured responses increase with higher temperature for all the test gases: propylene, ethylene, propane, methane, and hydrogen. This is due to increases in both the gas enthalpy and the quartz resonator response coefficient as the temperature rises. The response magnitude also increases with the number of carbon atoms in each target gas molecule as evidenced by the propylene (C3) and ethylene (C2) responses. In Fig. 7, the measured response to propylene gas is shown to decrease as the oxygen atmosphere becomes leaner and saturate in high concentrations of oxygen.

Figure 6. Measured frequency shift vs. temperature for a Pd:SiO₂-coated sensor exposed to 1% concentrations of propylene, ethylene, propane, methane, and hydrogen gases mixed with oxygen.

Figure 7. Measured frequency shift vs. oxygen concentration for 1% propylene gas flowing across a Pd:SiO₂-coated sensor. No response occurs for hydrocarbons in an oxygen-deficient atmosphere. The different plotted points (open circles and filled squares) represent values from two separate tests.

Again, this behavior is typical of calorimetric sensors.

However, based on the limited sensor measurements for these few test gases, the Pd:SiO₂ sensor response is somewhat atypical for a calorimeter. The olefins (represented by propylene) produce significantly larger frequency shifts than the paraffins (propane), ~ 20 times greater as seen in Fig. 6, and hydrogen sensitivity is relatively large compared to several of the hydrocarbons. Combustible gas detectors will also show some response to carbon monoxide in the presence of oxygen. But this sensor shows no reaction (although in an oxygen-deficient atmosphere at the highest temperatures, CO strips oxygen from the SiO₂ matrix, producing a small, but measurable, mass shift).

The palladium in the matrix obviously modifies the gas sensitivity and selectivity giving it an enhanced catalytic activity. Figure 8 shows the response of two sensors, one having only a surfactant-templated mesoporous SiO₂ thin film and the other with an identical SiO₂ film with palladium introduced in the matrix, exposed to a 1% propylene gas mixture. The virgin SiO₂ device shows a small reaction at the highest temperatures due to the large surface area of the porous film, but its response is much lower than that of the Pd:SiO₂-coated sensor. The exact dependence on the metal ions exchanged in the SiO₂ films is still under investigation; some limited work to date has shown that sensors with V, Cu, or Fe in the matrix exhibit no favorable hydrocarbon or hydrogen

Figure 8. Measured frequency shift vs. temperature for a propylene-oxygen mixture comparing the sensitivity enhancement due to Pd ion-exchange in the mesoporous SiO₂ thin film coatings.

catalytic reactivity and often have responses no larger than those for the SiO₂ film alone.

From measurements using the Pd:SiO₂-coated resonators, it appears that sensitivity to hydrocarbon detection may be greater than for other types of calorimeters. It is postulated that catalyzed combustion (and the associated temperature increase) in the porous films stress the resonator surface, producing a frequency shift much greater than that for an equivalent temperature shift in the bulk quartz (as illustrated in Fig. 1).

Utility of the surfactant-templated mesoporous silica sensors for vehicle exhaust monitoring depends on discrimination in the presence of other gas constituents. The Pd:SiO₂ devices exhibit no measurable response to NO or NO₂ at concentrations up to 9000 ppm, levels several times higher than expected in the exhaust stream. CO₂ elicits a small response (~ 20 ppm-Δf at 15% by volume concentration at 450 °C) due to a much larger heat capacity than the other test gases. Since CO₂ concentration in vehicle exhaust is usually near the values tested, it could interfere with detection of low levels of hydrocarbons. Water vapor, when exposed individually to the sensors, does not illicit a response. However, when water vapor is mixed into a propylene-oxygen stream at high temperatures (> 300 °C), a significant reduction in measured frequency shift (approx. a factor of two for 3 % H₂O) occurs. This reaction is unexpected as the difference in gas thermal conductivity alone does not account for such a large shift in response from a small concentration of water. Some of the shift in response magnitude could be an anomaly of the measurement system, and the phenomenon is still being studied. If proved real, the interference from water vapor would be detrimental to eventual sensor implementation.

A comparison of responses for the Pd:SiO₂-coated resonators when exposed to all the test gases is given in Table 1. Sensitivities are listed for only one specified temperature and gas concentration.

CONCLUSIONS

TSM quartz resonators coated with thin films of mesoporous silica and ion-exchanged with palladium ions have shown good sensitivity and selectivity for high-temperature detection of hydrocarbon gases in the presence of oxygen. The sensors act much like calorimeters responding to slight temperature increases produced by catalyzed combustion in the high surface area films. Additional investigations are in progress to determine catalytic specificity provided by different metal ions in the silica matrix and to further understand interference effects from water vapor.

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Table 1. Comparison of Pd:SiO₂-coated resonator response for various gases at specified temperatures and concentrations.

Gas	Temp (°C) / Conc. (%)	Sensitivity (ppm-Δf)/(ppm-gas)	Comments
Propylene (C ₃ H ₆)	450 / 1	5.4 × 10 ⁻²	due to catalytic combustion in O ₂
Ethylene (C ₂ H ₄)	450 / 1	2.4 × 10 ⁻³	"
Propane (C ₃ H ₈)	450 / 1	2.1 × 10 ⁻³	"
Methane (CH ₄)	450 / 1	< 5 × 10 ⁻⁴	too small to quantify
Hydrogen (H ₂)	450 / 1	3.8 × 10 ⁻²	due to catalytic combustion in O ₂
Carbon Monoxide (CO)	450 / 1	~ 1 × 10 ⁻³	only in oxygen-deficient atmosphere
Carbon Dioxide (CO ₂)	450 / 15	2.7 × 10 ⁻⁴	due to higher specific heat
Nitric Oxide (NO)	450 / 0.5	none	
Nitrogen Dioxide (NO ₂)	500 / 0.9	none	
Water Vapor (H ₂ O)	400 / 3	< 5 × 10 ⁻⁵	anomalous response in mixtures