Metal-coated Glass Microfiber for Concentration Detection in Gas Mixtures using the 3-Omega Excitation Method

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ABSTRACT

The 3-Omega measurement technique was applied to a fabricated metal-coated glass fiber for the purpose of low power gas sensing. The sensor performance was evaluated for mixtures of CO₂, Ar, He and CH₄ in N₂ in an isothermal chamber, where mass flow controllers precisely controlled concentrations. The metal-coated fiber was fabricated by depositing a thin layer of gold (~150 nm) onto a glass fiber, using a custom designed deposition lathe installed in a standard sputtering system. A custom 3-Omega conditioning circuit controls the AC heating current and detection of the 3-Omega voltage signal. The amplitude and phase lag, and the in-phase and out-of-phase components of the 3-Omega voltage signal are presented for different gas mixtures and are related directly to their concentrations. Using this gas sensing technique, we have demonstrated the uncertainty in concentration (i.e., sensitivity) to be better than 50 ppm, and as low as 10 ppm for some gases. The dependence of the different 3-Omega signals on the thermophysical properties of the system is briefly described. The low power, high sensitivity nature of the sensor is also demonstrated as the metal-coated fiber sensor consumes ~ 10% of the power consumed by conventional thermal conductivity detectors (TCDs), and unlike those, it operates at near room temperatures.

KEYWORDS

3-Omega technique; Low power gas sensing; Thermal Conductivity Detector (TCD); Metal-coated glass fiber; AC excitation

1. Introduction

Gas sensors have been widely used to determine the composition of gas mixtures and to detect the presence of a particular species in gases. [1] Thermal conductivity detectors (TCDs) are a common type of gas sensors, which use the difference in thermal conductivity of gases to detect the composition of gas mixtures. Miniature TCDs are highly desirable for gas chromatography due to their excellent sensitivity demonstrated to 1 ppm. Nanoscale bridge type sensors using nanotubes [2], nanowires [3], and nanobelts [4] have also been fabricated. These TCDs often require high power consumption (hundreds of milliWatts to a few Watts) to provide sensitivities in the few ppm range. Smaller variation of microTCDs are fabricated that offer better sensitivity and power consumption [5]. However some of these TCDs operate at high temperatures [6], which necessitate routine re-calibration and may be destructive to the detected

sample. More recently, we have demonstrated the ability to perform low power gas sensing using the 3-Omega technique on a polysilicon microbridge geometry while still maintaining good sensitivity [7]. However, in the microbridge design a significant portion of the heat was conducted along the microbridge to the substrate, which reduced the heat input to the surrounding gas medium, thereby limiting the sensitivity of 3-Omega technique to 1,000 ppm. Herein, we present a gas sensing technique that overcomes not only these challenges, but offers other advantages such as ease of fabrication, near room temperature measurements while still consuming power in the order of milliWatts. The design and fabrication technique of the sensor used in this work was first developed by Schiffres *et al* [8]. for the measurement of thermal conductivity of liquids and gases.

1.1 Principles of 3-Omega

The 3-Omega technique has been extensively used in thermal conductivity measurements [9] and is well described in literature [10], but it also offers an approach to low-power gas sensing that we have recently investigated. [7] In a standard 3-Omega measurement, a sinusoidal electrical current of amplitude I_ω at frequency $\omega=2\pi f$ is driven through a metal heater line, resulting in a Joule heating at frequency 2ω . The periodic heating creates a thermal wave that penetrates the surrounding medium. The thermal wave attenuates over a penetration depth, given by $L_p = \sqrt{\alpha/2\omega}$, where α is the thermal diffusivity of the surrounding medium. This gives rise to a temperature oscillation at the source, which has a frequency 2ω but lags the heating current by a phase lag ϕ due to the finite time it takes for a temperature response. The temperature oscillation causes the resistance of the heater to oscillate at 2ω . Since the current is driven at 1ω , this resistance oscillation results in a voltage component at 3ω . The amplitude, $V_{3\omega}$ and phase lag, ϕ of the voltage signal can be directly measured and the voltage amplitude can be directly related to the amplitude of temperature oscillation by Eq. (1).

$$\Delta T_{2\omega} = \frac{2}{dR/dT} \cdot \frac{V_{3\omega,\text{RMS}}}{I_{\omega,\text{RMS}}} \quad (1)$$

where dR/dT is the temperature rate of change of the sensor's resistance and the subscript RMS refers to the root-mean-square value.

The amplitude and phase signals can be directly related to the thermal properties (*e.g.*, thermal diffusivity) of the sensor and the gas medium. Since the thermal diffusivity is a function of the gas mixture, the 3-Omega signals vary with gas composition and can be used to resolve gas compositions. The phase lag is only a function of the geometry and thermophysical properties of the heater and its environment, and is independent of the amplitude of driving current thus uniquely alleviating the need for routine calibration.

2. The 3-Omega sensor

In our previous study on 3-Omega gas sensing, a polysilicon microbridge suspended on a silicon dioxide sacrificial layer was used which could readily resolve gas concentrations of 1,000

ppm in binary mixtures [7]. Since a significant portion of the heat was conducted within the microbridge and dissipated to the solid substrate, the sensitivity to the gas medium was limited. In this study, a glass fiber coated with a thin layer of metal (gold) is used as the 3-Omega heater and the sensing element. The raw glass fiber has a 26 μm diameter, and consists of a leaded glass core (Schott F2) and a borosilicate cladding (Schott 8250) [8]. The diameters and properties of the different layers are provided in Table 1.

2.1 Fabrication of sensor

The metal layer was deposited using a conventional sputtering system (Unifilm Multisource Sputtering System, IEN, Georgia Tech). To achieve uniform cylindrical coating, the fibers were strung tautly onto a spool, which was uniformly rotated with the motor in the sputtering system as shown in Fig. 1[8]. The deposition lathe ensured uniform circumferential coating. Since the deposition crystal monitor is calibrated for deposition in a rectangular plane, the thickness deposited on the sensors is smaller by a factor of π , which results from the ratio of the fiber's actual surface area ($\pi \times \text{diameter} \times \text{length}$) to its projected area ($\text{diameter} \times \text{length}$). The sputterer was programmed to deposit a 10 nm titanium adhesion layer, followed by a 150 nm of gold. The fiber was characterized using a SEM to determine the exact thickness and to verify the uniformity of the gold layer along the circumference of the fiber. This was done by measuring the metal layer's thickness at over 10 points along the fiber's circumference. The resulting thickness of the metal layer was 135 ± 11 nm (see Supplemental Information for more details). Figure 2 shows an SEM image of the fiber's cross section. Figure 3 shows a picture of the metal-coated sensor along with a schematic highlighting the electrical connections and a cross-section of the fiber.

2.2 Experimental set-up

The gold-coated fiber was placed in a dual-in line package (DIP) and wired in a four-point configuration. Electrical contacts to the fiber were made using DuPont© CB028 silver conductive paste. The sensor was placed in an isothermal chamber whose temperature was uniformly increased from 20 °C to 50 °C in 5 °C increments and the resistance's temperature dependence dR/dT was measured to be 0.1155 ± 0.008 ohm/°C (see Supplemental Information for details). An experimental set-up similar to the one described in our previous work was used [7]. An input current amplitude of 12 mA was used and frequencies were swept between 0.5 and 2000 Hz. 3-Omega measurements were carried out on mixtures of trace gases (He, Ar, CO₂ and CH₄) in N₂. The concentration of the trace gas was varied between 0 and 5% in increments of 0.5%. At each concentration, the amplitude (ΔT), phase lag (ϕ), and the in-phase (X) and out-of-phase (Y) components of ΔT from the SR850 lock-in amplifier were recorded (see Eq. (2) for analytical relationships). The measurements were repeated multiple times for each concentration and the resulting standard deviation was used to estimate the experimental uncertainty.

$$X = \Delta T \cos \phi \quad Y = \Delta T \sin \phi \quad (2)$$

3. Results and discussion

3.1 Raw signals

Figure 4 shows an example raw output signal of the 3ω measurements on the sensor in He-N₂ mixture for a current amplitude of 12 mA. Similar data and trends were observed for other gas mixtures (Ar, CH₄ and CO₂ in N₂, see Supplemental Information for data). The plots show the frequency dependence of (a) amplitude of temperature oscillation ΔT , (b) phase lag, as well as the (c) in-phase (X) and (d) out-of-phase (Y) parts of ΔT , respectively. As discussed in our previous work, the system can be approximated to be in quasi-steady state at lower frequencies with a large penetration depth, where the thermal transport is primarily governed by the thermal conductivity of the gas mixture. Table 2 summarizes the relevant thermophysical properties of the five gases used at room temperature [11]. Since He has a higher thermal conductivity than N₂, a system with higher concentration of He in N₂ dissipates heat better. This leads to a decrease in the amplitude of temperature oscillation as the concentration of He increases. The phase lag, however is most sensitive to gas concentration at frequencies near 600 Hz, which is the characteristic frequency of the sensor-gas system and also exhibits a maximum at this frequency. As discussed in our previous work [7], this characteristic frequency is related to the geometry and the thermophysical properties of the sensor-gas system. The phase lag describes the thermal response of the system and thus, is dictated by the specific heat of the gas mixture. Since He has a higher specific heat than N₂, a system with higher concentration of He in N₂ responds slower. This leads to an increase in phase lag as the concentration of He increases. The curves for X and Y exhibit similar trends to that of the amplitude, where the maximum sensitivity to gas composition is observed at low frequencies.

3.2 Composition curves

Based on the raw 3-Omega signals, composition curves are developed which can be used to determine the composition of an unknown mixture using the measured signal. These curves present the difference in the 3-Omega signal between the gas mixture and pure N₂ reference gas as a function of the trace gas concentration. Figure 5 shows the difference in 3-Omega signals (ΔT , ϕ , X and Y) between the He-N₂ mixture and pure N₂ as a function of frequency for different concentrations of He. Similar curves were obtained for the other mixtures as well (see Supplemental Information). As mentioned before, ΔT , X and Y are most sensitive to concentration at low frequencies while phase lag exhibits better sensitivity near the characteristic frequency. To better study the effect of mixture composition on this differential 3-Omega signal, we consider the differential ΔT , X and Y between the frequencies 3 and 10 Hz to focus on the range of most sensitivity. These regions of maximum sensitivity are highlighted in the Fig. 5. We use the average over these 10 points instead of a single point (frequency) to smooth over (noise) fluctuations. These average values are then plotted against mixture concentration for all gas mixtures to obtain composition curves based on ΔT , X and Y , which are depicted in Figs. 6(a), (c) and (d), respectively. A linear fit between the differential signal and concentration was

performed and serve as the composition curves for the sensor. A similar analysis was carried out on the phase lag where the frequency range between 200-900 Hz was used; this range contains the characteristic frequency and exhibits the highest sensitivity. The corresponding composition curve is shown in Fig. 6(b). Using these composition curves, it is possible to determine the composition of an unknown binary mixture based on the differential 3ω signal.

To determine the sensitivity of the sensor, an uncertainty analysis was carried out on the composition curves. Eq. (3) can be used to calculate the uncertainty in concentration, where $\delta(\text{signal})$ is the uncertainty in the measured 3ω signal and m is the slope of the composition curve based on the corresponding signal. The uncertainty of the measured signals was calculated from the standard deviation between multiple 3ω measurements using Student's t-distribution. The composition curve is highly linear ($R^2 = 0.99$) and the slope is well characterized ($m=0.143\pm0.003$, from 95% confidence interval), therefore uncertainty in the slope does not significantly add appreciable uncertainty to the composition uncertainty. The analysis is similar to the one presented in our previous work [7]. Table 3 lists the uncertainty in the concentration for the different gas mixtures. As can be seen from Table 3, the composition curve based on ΔT generally provides the best sensitivity in concentration. The composition curve based on ϕ , while it has the worst sensitivity remains unchanged regardless of the input current. This is beneficial because it removes the need for routine sensor calibration.

$$\delta(\%) = \left| \frac{\sqrt{2} \cdot \delta(\text{signal})}{m} \right| \quad (3)$$

It is also possible to determine the minimum detectable concentration of the gases based on the composition curves using Eq. (4), where c is the y-intercept of the composition curve. Table 4 summarizes this minimum concentration for different gas mixtures, based on each of the four 3ω signals.

$$\text{Min \%} = \delta(\%) + \left| \frac{c}{m} \right| \quad (4)$$

As can be observed, it is possible to detect gases with uncertainties in measurement (*i.e.*, sensitivities) lower than 10 ppm for gas mixtures of components with thermophysical properties differing by an order of magnitude (*e.g.*, He and N₂). For mixtures of components with similar properties (*e.g.*, CH₄ and N₂), the sensitivity is ~50 ppm; improved sensitivity to this gas can be achieved by using a different reference gas when properties are similar (*e.g.*, use He instead of N₂ when measuring CH₄).

3.3 Thermal Conductivity Sensing

Schiffres *et al.* [8] developed a generalized n -layer concentric cylindrical periodic heating solution and applied it to determine the thermal conductivity of gases using a similar metal-coated fiber heater approach; caution needs to be used when applying the mathematic model presented by Schiffres *et al.* as a few minor mathematic errors are present in the publication (see Supplemental Information corrections). The amplitude data (ΔT) was fit to the model to

determine the thermal conductivity of our mixture for different gases and concentrations. Figure 7 shows the thermal conductivity as a function of the concentration of the trace gas in the mixture. These curves provide another way to quantify an unknown mixture based on its thermal conductivity, which does not require comparison to the 3ω signals of N_2 . However, it must be noted that the resolution based on the thermal conductivity sensing is significantly worse than that based on the other composition curves since this is based on a fitted model propagating error and not the direct 3-Omega signals themselves.

CONCLUSIONS

In this work, the 3-Omega technique was used on a metal-coated microfiber for low power, high resolution gas sensing at near room operational temperatures. The sensor was fabricated by sputtering on a custom deposition lathe. The phase lag signal exhibits a maximum at a frequency corresponding to the characteristic frequency of the system, where it exhibits the maximum sensitivity as well. Composition curves were developed for different gas mixtures based on each of the four output signals of the 3-Omega measurement. The composition curve based on phase lag is independent of the driving current, which eliminates the need for individual sensor calibration. Herein, we have shown that it is possible to determine gas concentrations with a resolution as small as 10 ppm. This sensitivity was achieved with a RMS power consumption of ~ 5 mW (determined using $P_{RMS}=I_{RMS}^2R$). This work offers the advantage of sensitivities that are comparable to some of the best commercial sensors, while consuming power that is two orders of magnitude lower. Furthermore, the maximum temperature reached by the sensor, which is the sum of the DC and maximum AC temperature rise during operation is ~ 25 °C. The AC temperature rise is directly related to the 3-Omega signal whereas the DC temperature rise is obtained indirectly from the change in resistance between zero current and a current of 12 mA, and the sensor's dR/dT . This temperature rise is significantly less than other thermal conductivity gas sensors that require elevated temperatures (~ 100 °C) for high sensitivities. This results in improved sensor lifetime and reduces the frequency of calibration. Furthermore, the fabrication of the metal-coated fiber is simpler than microfabricated bridges, as it does not require photolithography. Finally, since the amplitude and phase lag are independent and governed by different thermal properties (*e.g.*, thermal conductivity and specific heat), it is now possible for this technique to be extended to ternary gas mixtures.

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	Layer 1^a (Schott F2 leaded glass)	Layer 2^a (Schott 8250 borosilicate)	Layer 3 (Titanium)	Layer 4 (Gold)
Diameter (d)/ Thickness (t)	d=24 μm	t=1.1 μm	t=10 nm	t=150 nm
Thermal Conductivity (W/m-K)	0.78	1.18	21.9	317
Density (kg/m³)	3600	2280	4500	19300
Specific Heat (J/kg-K)	557	720	522	129

^a Properties and dimensions were supplied by the manufacturer

Table 1: Dimensions and properties of the different layers of the metal-coater fiber sensor[8]. The values for the fiber layers were provided by the manufacturer and the properties of the titanium and gold layers are obtained from Ref. [11].

Figure 1: (a) Schematic showing the deposition lathe with fibers strung onto the rotating spool. The black arrows indicate the direction of rotation of the spool and the golden arrows indicate the direction of gold sputtering. A bevel gear is used to convert the plane of rotation from the default horizontal plane to the vertical one with the spool. (b) A picture of the deposition lathe used.

Figure 2: (a) The cross-sectional image of the metal-coated fiber highlighting the gold layer. (b) A magnified image of the gold layer on the fiber. The uniformity of the coating was verified by measuring the thickness of the gold at several points along the circumference. An Energy Dispersive X-Ray Spectroscopy (EDS) study was also carried out on the fiber to verify the gold thickness.

Figure 3: A picture of the metal-coated fiber sensor with its electrical connections along with a schematic. Also shown is a cross-sectional schematic of the fiber indicating the dimensions of the fiber and the metal layer.

Figure 4: The raw 3-Omega signals for the He-N₂ mixture, for six different compositions, and a current amplitude of 12 mA. Figures (a) and (b) indicate the amplitude and phase lag, while (c) and (d) indicate the in-phase (real) and out-of-phase (imaginary) components of the amplitude, respectively. The amplitude, X and Y are most sensitive at low frequencies whereas the phase lag is most sensitive at a frequency close to the characteristic frequency of the system. The phase lag also exhibits a maximum at a characteristic frequency of the system.

Material	Thermal Conductivity (W/m-K)	Density (kg/m³)	Heat Capacity (J/kg-K)	Thermal Diffusivity (m²/s)
Nitrogen	0.0258	1.123	1041.8	2.21×10^{-5}
Methane	0.0346	0.644	2235.8	2.40×10^{-5}
Helium	0.1560	0.160	5193.0	1.87×10^{-4}
Argon	0.0177	1.603	521.5	2.12×10^{-5}
Carbon dioxide	0.0168	1.773	852.5	1.11×10^{-5}

Table 2: Relevant thermophysical properties of the different gases used in this work. [9]

Figure 5: Differential signals of amplitude, phase, X and Y vs. frequency for different compositions of He in N_2 . The sensitivity of the different signals at different frequencies can be readily noticed. The frequency range of high sensitivity considered for the composition curves is highlighted in each of the four figures.

Figure 6: Composition curves for all four gas mixtures based on differential 3-Omega signals. A linear trend between the averaged differential signal and concentration is observed for all cases, as indicated by a linear fit for the data. The composition curve based on phase lag is independent of driving current amplitude and eliminates the need for calibration for individual experiments.

Gas Mixture	Uncertainty in measured concentration using			
	ΔT (ppm)	ϕ (ppm)	X (ppm)	Y (ppm)
Ar in N ₂	18.7	916.4	43.3	22.9
He in N ₂	8.1	801.0	6.8	8.5
CH ₄ in N ₂	29.9	756.1	39.0	47.0
CO ₂ in N ₂	35.6	2400	32.7	37.9

Table 3: Uncertainties in the measured concentration (*i.e.*, sensitivity) of different gases for different composition curves

Gas Mixture	Minimum detectable concentration using			
	ΔT (%)	ϕ (%)	X (%)	Y (%)
Ar in N ₂	0.289	0.527	0.0927	0.281
He in N ₂	0.0869	0.145	0.0449	0.0846
CH ₄ in N ₂	0.0556	0.310	0.556	0.684
CO ₂ in N ₂	0.497	0.351	0.271	0.324

Table 4: Minimum concentration of different gases that can be detected based on the composition curve used

Figure 7: Thermal conductivity of different gas mixtures obtained by fitting the measured amplitude data to a standard heat transfer model for our sensor-gas system. This composition curve allows for determination of the concentration without relying on measurements of base gas.