A HARSH ENVIRONMENT, MULTI-PLASMA MICROSYSTEM WITH PRESSURE SENSOR, GAS PURIFIER, AND CHEMICAL DETECTOR

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ABSTRACT

A system for gas phase chemical detection in harsh environments has been developed that utilizes three microplasma-based devices: pressure sensor, gas purifier, and optical emission sensor. The devices all utilize microplasmas between thin-film electrodes and occupy a combined active area of 10.5 mm^2. They are fabricated on glass chips and enclosed in a 0.33 cm^3 ceramic package. The optical emission sensor operates by fractionating and exciting gas species for chemical spectral detection. The pressure sensor measures the change in microplasma current distribution with pressure, and achieves a sensitivity of 9800 ppm/Torr at 200°C. The gas-purifying microscale sputter ion pump purifies the environment by selectively removing nitrogen and oxygen, and achieves a 56.5x reduction in nitrogen concentration relative to helium. This purification enhances the ability to detect trace amounts of gases. As a validation of this system, a spectral enhancement of 8x at 200°C for carbon line emission intensity relative to nitrogen has been demonstrated.

I. INTRODUCTION

The cost of drilling for petroleum exploration, field development, and long-term geological monitoring can potentially be reduced through the use of micro-holes and MEMS sensors [1]. Numerous interferometric fiber optical sensors have previously been used to detect temperature and pressure down-hole [2]. During petroleum exploration and pumping, the flow of removed material is a combination of oil, water, and gases. Continuous down-hole analysis of gas during petroleum pumping is useful for the control of product quality, the detection of unwanted contaminants, and the optimization of product treatment downstream [3]. Continuous chemical analysis is also useful during petroleum detection. The down-hole sensors for detection and monitoring must be able to withstand elevated temperatures and pressures. They also must be able to detect carbon, sulfur-containing gases, and contaminant gases such as H_2S and CO_2 [3, 4].

A microscale gas chemical detection system capable of operating at high temperatures requires a number of durable components. Devices utilizing microdischarges between durable thin film electrodes are attractive as they can operate at high temperatures. Microplasmas can be miniaturized to chip scale for chemical sensing and multiple other applications [5]. A microdischarge-based spectroscopic sensor [6] provides a viable chemical detection mechanism in harsh environments. However, several additional elements are needed for this application. Purification of a gas sample can become necessary as small amounts of nitrogen dominate emission spectra with intense line emissions [7]. For this purpose a microplasma-based gas-purifier (that removes modest quantities of oxygen
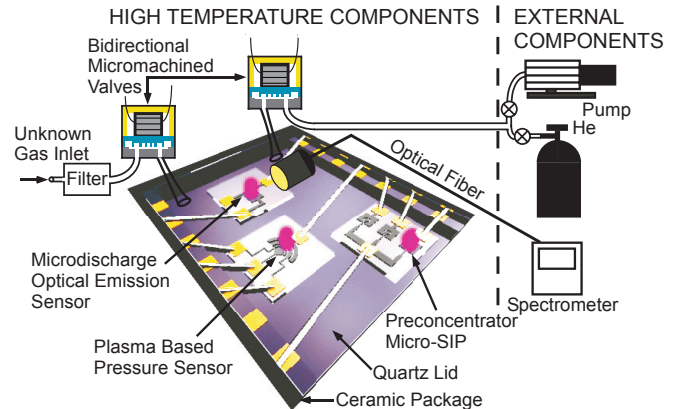
Fig. 1: Schematic of the entire system. The plasma-based pressure sensor, gas purifying micro-SIP, and chemical detector are enclosed in a ceramic package with a quartz lid. Micromachined valves allow a sample of gas to enter, isolating it for purification and sensing after backfilling with a carrier gas to the desired pressure.

and nitrogen) is utilized. A high-temperature microplasma-based pressure sensor (that minimizes packaging challenges presented by alternatives) is also included.

This paper describes a gas chemical detection system composed of microplasma-based devices which operate together in harsh environments to isolate a gas sample, selectively remove unwanted gas components, and detect the possible presence of a desired or contaminant gas. The operation of the individual devices and their combined operation in a single package are presented.

II. SYSTEM CONCEPT AND OPERATION

A planar micromachined pressure sensor, gas purifier, and gas chemical detector are hermetically sealed inside a ceramic package with a quartz lid to prepare and sense the gas sample (Fig. 1). Micromachined valve(s) control the gas flow into and out of the package.

A. Pressure Sensor The pressure sensor uses the novel approach of measuring the change in spatial current distribution of a microplasma with pressure. As pressure varies, the mean free path of ionized gas molecules changes and consequently, the discharge and current distribution vary. With increasing pressure, microplasma discharges become more confined due to the shortening mean free path of ions. This results in more current between closely spaced electrodes. To measure the confinement of the current distribution, a single circular planar anode is partially surrounded by concentric cathodes as shown in Fig. 2a. Measuring the current in each cathode gives the spatial current distribution as a function of pressure. This
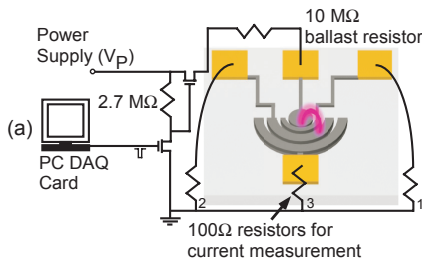
Fig. 2(a): Plasma-based pressure sensor used to determine when the system is ready for gas purification. Pulses are applied, and initial discharge current is monitored to determine pressure.
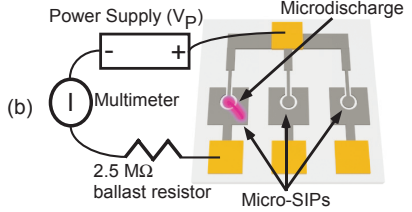
Fig. 2(b): Gas-purifying micro-SIPs. A dc voltage is applied to selectively remove nitrogen and oxygen while leaving carbon and helium.
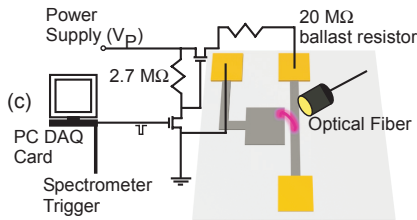
Fig.2(c): Microdischarge optical emission sensor (chemical detector) used to detect carbon and other vapors through recorded spectra.

allows the pressure to be determined based on the distribution after sensor characterization. The spatial current distribution of microplasmas has previously been shown to vary with pressure from 1.2-10 Torr [8]. Multiple cathodes and a single anode are used in the pressure sensor, as opposed to multiple anodes and a single cathode, as the cathode current was shown to vary less dramatically with pressure changes [8]. This increases the identifiable pressure range.

To obtain consistent results, pulsed microplasmas are used in the pressure sensors. At lower pressures ($\approx$ <100 Torr), a dc current can be measured in the discharges, but as the pressure increases, sporadic current pulses are observed which make measurements difficult. These plasma variations are induced by factors such as heating, electrode wear, and re-deposition. To overcome this, relatively short current pulses are applied to create the microdischarges. These pulses result in one measurable current pulse per discharge, allowing pressure measurements at a set frequency.

B. Pump The gas-purifying micromachined sputter ion pump (micro-SIP) operates by sputtering titanium, bonding this titanium to gas molecules, and removing these molecules from the environment. The sputtering is caused by a dc microplasma between two titanium thin-film electrodes as shown in Fig. 2b. Micro-SIPs have previously been shown to reduce the pressure in a sealed cavity [9], but their ability to purify a gas environment has not been evaluated. Sputtered titanium has been shown to react selectively with nitrogen and oxygen [10] on the macroscale without interacting with helium, carbon, sulfur, and other gases of interest.

C. Detector The optical emission chemical detector operates by fractionating and exciting a gas species, using a pulsed microdischarge, which produces a spectral output that is characteristic of its energy transitions. The discharge is created between a thin-film anode/cathode pair as shown in Fig. 2c. An optical fiber directly opposite the microplasma, outside the quartz lid, couples the emitted light to a spectrometer (USB2000 from Ocean Optics Corp.). Pulsed discharges have

significant afterglow periods, and integrating both the afterglow and initial discharge emissions improves the signal to noise ratio [6]. The recorded spectra are examined to determine the unknown gas composition, based on the characteristic line spectra produced by individual gases.

D. Valve Bidirectional micromachined valves control the flow of gas into and out of the package. The valves have a separate inlet and outlet. By actuating a PZT stack, a serpentine valve seat is depressed against a Pyrex glass wafer to block gas flow. A thorough description and test results are presented [11].

The system utilizes these devices to isolate, purify, and sense a gas sample. One possible configuration for field use is shown in Fig. 1. Remote components, external to the harsh environment, include a gas pump, backfilling gas tank, and a spectrometer. In the proposed configuration, a sample is introduced into the empty package through one micromachined valve while a second connects the package to the external components for backfilling and pressure regulation. The internal microplasma-based pressure sensor monitors the pressure in the package, and when the desired pressure is reached, the package is isolated by closing the valves. The gas-purifying micro-SIP is then operated while the chemical detection sensor is pulsed, recording spectra over time. The micro-SIP continues to operate until the unwanted spectral line emissions caused by contamination are reduced enough to observe the spectral emissions created by the gas in question, if present.
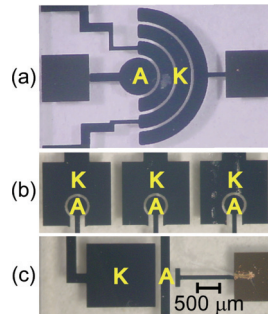
Fig. 3: Devices: (a) pressure sensor with a single anode and 3 cathodes, (b) gas purifying micro-SIPs, (c) chemical detector.
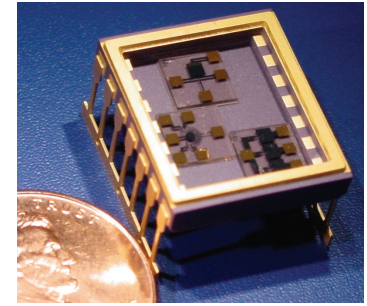
Fig. 4: System before sealing in ceramic package next to a U.S. penny. The combined area of the chips is 75 mm^2.

III. DESIGN AND FABRICATION

A. Pressure Sensor One microplasma-based pressure sensor was designed with a single anode surrounded by three semicircular cathodes as shown in Fig. 3a. The cathodes' spacing and widths were theoretically determined using the spark breakdown voltage of parallel-plate electrodes in air for the pressure range of interest [12]. Cathodes were arranged so that as the mean free path of the sampled gas decreased, the fractional area of the farthest cathode nominally reachable by ions in avalanche breakdown decreased. For example, initial breakdown theoretically ceases to occur between the anode and the farthest cathode in the displayed sensor at 133 Torr. However, secondary electron emissions from the other cathodes continue to ionize surrounding gases and potentially cause the current to saturate at pressures exceeding this threshold in the farthest cathode. The sensors were designed to function with an applied voltage of 1000 V, but altering the voltage would result

in different sensitivities. Having three cathodes, as well as relatively large cathode areas, resulted in greater sensitivity than similar designs with five cathodes. Of the tested designs, the cathodes with the highest sensitivity were 300 μm in width and had gaps of 50 μm between them. Other designs tested had 35-μm-wide cathodes and 35-μm gaps, or 50-μm-wide cathodes and 50-μm gaps. Semi-circular concentric cathodes were used as they demonstrated a higher sensitivity than straight cathodes. A computer-controlled circuit determined the discharge duration. A current limiting 10-MΩ ballast resistor was used and 100-Ω resistors were used in series with each cathode to measure current.

B. Pump The gas purification micro-SIPs were designed with circular anodes surrounded by large cathodes as shown in Fig. 3b. The cathodes were larger than the anodes as the positive ions primarily sputter the cathodes, leaving the anodes intact. Up to three anode/cathode pairs were included in each system to provide for extended periods of purification and multiple uses. The electrodes were fabricated from titanium as it has the ability to bond with nitrogen and oxygen, while failing to do so with helium and carbon. The cathodes had an area of 1.52 mm^2 and discharge gaps of 50 μm. A dc voltage of 1000 V was applied to induce rapid purification, and a 2.5-MΩ ballast resistor was used.

C. Detector The optical emission chemical detectors were designed with a single anode/cathode junction and large cathodes as shown in Fig. 3c. As microplasmas have been shown to be confined over the cathode, relatively large cathodes, 1.82 mm^2, were used to produce a large glow region for improved optical emission detection. A 100-μm discharge gap separated the electrodes and a voltage of 1000 V was applied. Computer-controlled pulses triggered the discharges and spectrometer. A 20-MΩ ballast resistor was used.

All three microplasma-based devices were fabricated on a single wafer with two masks to simplify processing. A Ti film (1 μm thick) and an Au film (500 nm thick) were thermally evaporated onto a glass wafer (500 μm thick) without removing the wafer from vacuum. The contact pads were patterned on the gold layer using photolithography and etched using Transene GE-8148 gold etchant, which does not etch titanium. The electrodes were then patterned in the titanium layer using photolithography. The final devices had a footprint of 25 mm^2 each. Solder and epoxy were used to connect the devices and seal the package.

IV. RESULTS AND DISCUSSION

A. Pressure Sensor Pressure sensors were packaged and tested with the gas sampling devices in ceramic packages at 200ºC. Voltage pulses with durations of 20 ms were applied to the pressure sensors at a frequency of 2 Hz, although higher frequencies are possible. The applied pulses resulted in measurable current pulses through each cathode, approximately 50-200 ns in duration. The average amplitude of 100 current pulses in each cathode was obtained at different pressures. These cathode currents divided by the total current, i.e. the percentage, was used to define the current distribution. The fractional current is used to compensate for the temperature coefficient of the normal current.

The pressure sensors were designed to operate around 200 Torr and with different sensitivities, but could be designed to operate around different pressures. The operating pressure of
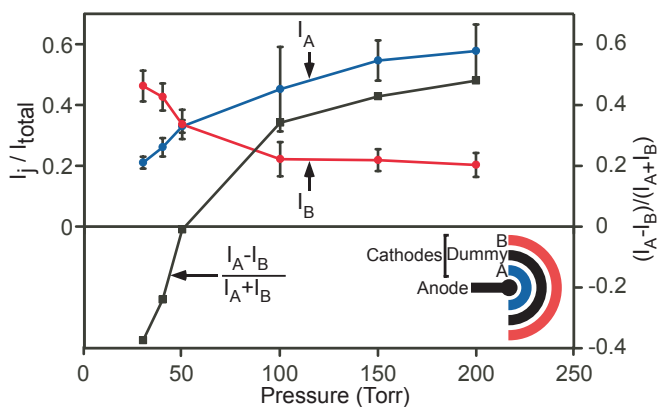

Fig. 5: Average current distribution of 100 consecutive measurements used by the pressure sensor to measure pressures between 30 and 200 Torr at 200°C. (I_A is current from cathode A and I_B is current from cathode B.) The error bars indicate a standard deviation.

200 Torr was chosen as the micro-SIPs are able to purify for days at this pressure without completely sputtering the cathodes.

Figure 5 shows a typical current distribution and sensitivity of a pressure sensor using 300-μm cathodes with 50-μm gaps between them at 200ºC. The sensitivity is calculated using the difference over the sum of the current percentage in two cathodes. In this sensor design, current flows through all three cathodes while the sensitivity is measured between the closest and farthest cathodes from the anode. The center cathode acts as a dummy cathode, used to maintain a uniform microplasma. This particular pressure sensor operates over 30-200 Torr, producing a sensitivity of 9800 ppm/Torr over 30-100 Torr and 1400 ppm/Torr over 100-200 Torr. At lower pressures, more current flows through the farthest cathode, due to the longer mean free path, while at higher pressures more current flows through the closest cathode. Pressure sensors having 50-μm-wide cathodes and 50-μm gaps produced relatively linear sensitivities of 2000 ppm/Torr over 25-275 Torr when examining the two cathodes closest to the anode.

B. Pump The gas purification provided by a micro-SIP in the package was evaluated by examining the spectra produced by the microplasma discharge over time. The strongest nitrogen and oxygen line emission intensities were normalized to that of helium to account for variations in discharge intensity. A micro-SIP was operated in an environment containing 99.25% helium (99.995% pure) and 0.75% air to test the purification
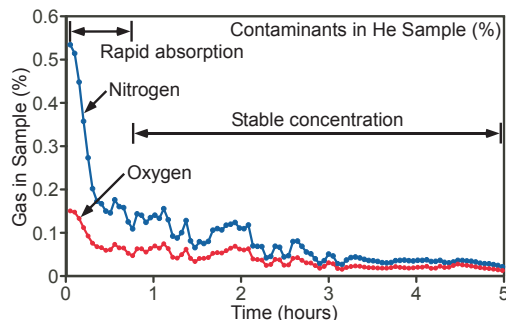
Fig. 6: Percentage of contaminants (nitrogen and oxygen) in helium sample during gas purification, showing the thorough removal of the unwanted gases. Helium is the most commonly used carrier gas in gas chromatography.
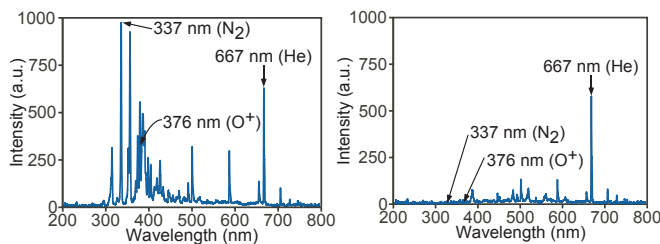
Fig. 7: Spectra of the pump discharge in 99.25% helium with air contamination at 200 Torr (a) before purification and (b) after purification. Small amounts of N_2 cause intense line emissions compared to He at time = 0.
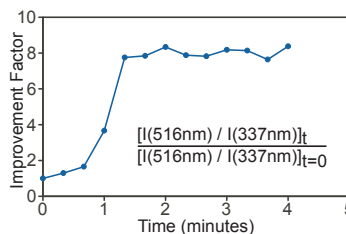
Fig. 8 (left): Ratio of carbon to nitrogen emission intensity during gas purification at 200°C, based on the strongest line emissions. The starting value is 1. This indicates the increased ability to detect carbon with respect to contaminants. Acetone is the sampled vapor.

abilities at 200 Torr. A 56.5x reduction in nitrogen and a 16.2x reduction in oxygen were observed over five hours as shown in Fig. 6. The final concentrations of the contaminant gases, based on the emission intensity, were 90 ppm and 70 ppm, respectively. Figure 7 shows a spectrum produced before purification and one after purification. The nitrogen and oxygen emissions were almost completely removed while a helium emission remained, indicating that helium was not removed to a detectable extent. Nitrogen and oxygen produce strong line emissions despite their relatively low concentrations, thus making it advantageous to remove these emissions when detecting other gases.

For the overall system, preliminary testing was performed at 200°C based on anticipated requirements [13], although it can potentially operate at much higher temperatures. The set-up for this testing utilized only one micromachined valve, through which both the sample and backfilling gas were introduced. Acetone vapor, 10,000 ppm, was introduced as a carbon source and helium was used to backfill the system to a final pressure of 200 Torr. The system was raised to 200°C and the optical emission sensor was operated every 20 seconds to determine gas concentrations based on emission intensities. The sensor was operated for 50 ms and the emissions were integrated for 300 ms to capture the afterglow. The micro-SIP
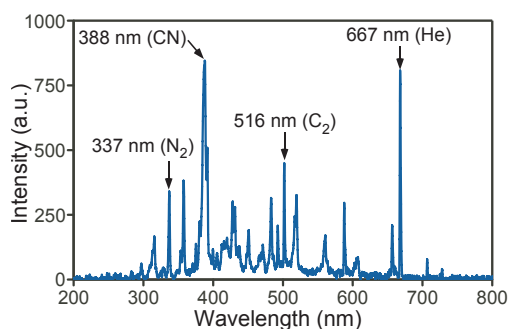
Fig. 9: Spectra of acetone sample backfilled with helium during gas purification at 200°C, showing diminished nitrogen and increased CN and C_2 emissions.

was activated and the strongest carbon emission (516.4 nm) increased in intensity by 8x (Fig. 8) relative to strongest nitrogen emission (337.1 nm). This purification increased the ability to detect carbon with respect to the contaminant gases. Figure 9 illustrates the resulting spectra after purification where the carbon and CN emissions are much stronger than the contaminant nitrogen.

V. CONCLUSION

The chemical detection system is capable of purifying a gas sample for the purpose of carbon detection at temperatures of at least 200°C. Only two masks are required to fabricate the primary devices. The microplasma-based pressure sensors were capable of operating at this elevated temperature and obtained a maximum sensitivity of 9800 ppm/Torr. Gas-purifying micro-SIPs removed contaminant gases and demonstrated a 56.5x reduction in nitrogen emission intensity relative to helium. The complete system was able to detect carbon, and potentially other gases, at 200°C through increasing the strongest carbon emission by 8x relative to the strongest nitrogen emission.

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