Printed Gas Sensors for the Trillion Sensor Universe


*KWJ Engineering, Inc.
8430 Central Avenue, Ste. 2C, Newark, CA 94560, jrstetter@gmail.com

**SPEC Sensors, LLC
8430 Central Avenue, Ste. 2D, Newark, CA 94560, sales@spec-sensors.com

ABSTRACT

We discuss two next generation, very small, microwatt power gas sensor platforms: Printed Electronics and MEMS. The resulting new sensors, a printed amperometric gas sensor (SPEC™) utilizing nanoparticulate catalysts and a MEMS thermal conductivity nanosensor (nanoTCD), are designed for modern and emerging applications requiring very low power consumption and small size that fulfill the vision of trends toward ubiquitous sensing. This paper describes the principles behind the two platforms and shows examples of each to highlight unique capabilities.

Keywords: printed electronics, gas, sensor, MEMS, thermal, electrochemical

1 INTRODUCTION

There are billions of physical sensors now in place for temperature, pressure, acceleration, and other parameters in consumer, medical, automotive, and industrial devices. Devices used for the benefit of consumers and by our societal infrastructure have created high volume markets for sensors. Chemical and gas sensors face an uphill challenge in joining this paradigm, because current technology is not able to meet the cost-size-power-performance targets for high volume distributed sensing applications. Our innovative approach combines printed electronics manufacturing capability with nanotechnology for gas sensing to enable a disruptively designed sensor platform for many important gases including carbon monoxide (CO), ethanol, oxygen (O₂), ozone (O₃), nitrogen oxides (NOₓ), sulfur oxides (SOₓ), hydrogen sulfide (H₂S), chlorine (Cl₂), hydrogen (H₂), carbon dioxide (CO₂) and others. This new approach and innovative product line can bridge the cost-performance gap that is hindering ubiquitous applications with conventional sensor designs.

It is relatively easy to see large scale platform distribution, like the cell phone, bringing electronics and computational/connective powers to the individual. It is also relatively easy to see the need for sensory data to provide awareness of health, environment, danger, comfort, safety, security, and well-being. Therefore, there is a clear driver for trillions of chemical sensors since we have a need for information and awareness that is spatial, temporal, and personal in chemical dimensions. The diversity of the chemical dimensions, however, leads to difficult challenges:

- Adequate selectivity includes differentiating from hundreds and sometimes thousands of similar stimuli.
- Sensor specifications are often heterogeneous: one sensor cannot serve the fragmented applications space.
- Volume deployment creates challenges for new materials and low cost manufacturing approaches.
- Connecting the sensory data to the needed information (knowledge creation algorithm) is often absent.

Markets for chemical sensors include the billions of cell phones used as platforms for personal environmental measurements and controls. Also, the 132 million homes in the USA have multiple appliances, there are more than 100 million miles of pipelines, and 55 million gas meters in North America. There is 2-5 times more VOC [volatile organic chemicals] exposure indoors than outdoors. CO₂ sensors are needed for HVAC and comfort control in homes and businesses. Methane sensors are required for stoves/homes, fracking operations, and transport pipelines. CO sensors for safety have become law in many states.

Several emerging manufacturing technologies are available that can transition chemical sensors into the trillion sensor universe. The examples of printed and MEMS sensors are unique, not only for their improved performance, but also for their low cost manufacturing approach. These sensors will allow integration of high volumes of gas sensors within the eight exponential technologies that include biotechnology and bioinformatics, computational systems, networks of sensors, artificial intelligence, and the Internet of Things.

Figure 1. Printed amperometric gas sensors (left) and nano thermal conductivity sensor (right).
intelligence, robotics, digital manufacturing, infinite computing, medicine, and nanotechnology. The explosion of innovation for such applications will arrive when these sensors are generally available as “appcessories” for virtually anyone, as simultaneously low-cost, long-life, low-power, high performance, and tiny. The characteristics and technology for new printed sensors and novel MEMS thermal sensors, illustrated in Figure 1, are presented.

2 PRINTED SENSORS: BACKGROUND AND INNOVATION

SPEC Sensors, LLC’s, Screen Printed Electrochemical Sensor technology [1] (SPEC Sensor™) revolutionizes the current state of the art in amperometric gas sensing, enabling new applications in consumer and industrial safety monitoring. SPEC’s printed sensors offer the performance of the best quality electrochemical sensors at a fraction of the price. With ultra-thin design, SPEC sensors offer easy integration into wireless, portable, and networked or distributed sensing, making them ideal for health, environmental, industrial, and residential monitoring.

Features and Advantages:
- Smallest Form Factor: 3 mm thin, 15x15 mm square.
- High sensitivity, fast response time, stable over wide temperature, pressure and relative humidity ranges.
- 10 year lifetime for remote/extended monitoring.
- Microwatt power for long life battery or energy harvesting operation.

The form factor fits within 0.1 in³, and makes possible a broad range of new measurement applications, not just for one gas, but several, with an array of sensors. Sensors are available for CO, H₂S, and ethanol. Sensors for O₃, NO₂, H₂, and NH₃ are in development [2-6].

3 PRINTED AMPEROMETRIC GAS SENSORS: EXAMPLES

3.1 Carbon Monoxide

Carbon monoxide is the most ubiquitous toxic by-product of modern living. CO emissions result from residential, industrial and transportation activities and wherever combustion occurs. The tiny size and thin electrolyte layer of the SPEC sensor provides extremely fast response time (t₉₀ <15 seconds), as shown in Figure 2. SPEC CO sensor performance compares favorably with the best commercial CO sensors, as shown in Figure 2. With linearity up to 10,000 ppm, high sensitivity, detection limits of less than 1 ppm, and stability in typical environments measured in years, SPEC reaches distributed volume markets with high performance.

KWJ is developing a full line of printed amperometric sensors based on the SPEC design. Some of these are described in the following sections.

Figure 2. Printed gas sensor response for 50 and 100 ppm CO in air at 25 °C. Comparison of new SPEC design and conventional R Series KWJ commercial sensor.

3.2 Hydrogen Sulfide, Nitrogen Dioxide and Ozone

Hydrogen sulfide (H₂S), nitrogen dioxide (NO₂) and ozone (O₃) are other important gases that figure prominently in industrial safety and the atmospheric environment.

Figure 3. Response of 6 SPEC sensors to 0 - 20 ppm H₂S.
Our hydrogen sulfide sensor is designed to measure hydrogen sulfide up to 50 ppm. Figure 3 shows the response of 6 sensors for 0-20 ppm H\textsubscript{2}S.

NO\textsubscript{2} may also be measured in the 0-20 ppm range, as shown in Figure 4.

![Figure 4](image)

**Figure 4.** Response of 8 SPEC sensors to NO\textsubscript{2} between 0 and 20 ppm in air.

We have also developed printed, amperometric ozone sensors, designed to measure from 0-20 ppm ozone, with 10 ppb level sensitivity (Figure 5). Alcohol sensors as well as O\textsubscript{2} and SO\textsubscript{2} have already been prototyped.

![Figure 5](image)

**Figure 5.** SPEC sensor responses to O\textsubscript{3} at 0 – 250 ppb.

4 NANO-TCD GAS SENSORS: BACKGROUND AND INNOVATION

Concurrent with the development of the SPEC printed gas sensors, KWJ has developed a new thermal conductivity sensor platform for ultrafast, ultralow power gas measurements [7,8]. The MEMS nanoTCD is an extremely small, extremely fast, manufacturable, ultralow power, low cost, high reliability and long service life device. These microsensors are inherently suitable for modern, smart, microprocessor controlled gas monitoring applications.

![Figure 6](image)

**Figure 6.** Individual TCD die wire bonded and mounted to a 20 pin DIP. The thermal element at right is 1 x 50 \(\mu\)m.

The MEMS nanoTCD sensor platform consists of an array of 8 individually addressable, microfabricated, suspended, thermally isolated sensor elements (Figure 6). These are heated to a specified temperature by constant voltage or constant current control circuit. The thermal conductivity of the air surrounding the device will depend on the constituent gases present. This will be reflected in the rate of cooling and equilibrium temperature of the sensor element. The thermal response can then be used as a signal calibrated to gas concentration, e.g., CO\textsubscript{2} or CH\textsubscript{4} in air. When a large or increasing amount of a gas is present in the air above typical background levels, this measurement can be used to indicate poor air quality (e.g., for CO\textsubscript{2}) or the presence of a dangerous gas leak (e.g., for CH\textsubscript{4}). The sensor signal will be proportional to the analyte concentration and this information can be used to, for example, direct an HVAC system to supply fresh air as needed to restore air quality to acceptable levels or to alarm for a dangerous level of a toxic or flammable gas. The basic sensor can be operated as a simple pulsed-TCD element, or these elements can be post-processed to add functional layers to create sensors with chemical selectivity.

The sensor element has demonstrated more than 30 billion consecutive gas sensing measurement cycles in our lab, without a failure and without drift. This accelerated performance testing level predicts that the sensor will meet the specification of >5-10 years without calibration, which cannot be met by any other sensor on the market. Each measurement cycle uses an average power of less than 330 \(\mu\)W, making it the only available technology that is tiny and compatible with modern, wireless and power scavenging operation. It also has the advantage of compatibility with MEMS fabrication, with a tiny footprint and low cost. Additionally, due to low thermal mass, the sensor element responds quite quickly, with a time constant on the order of microseconds[8]. The fast response translates into low power measurements and means that many measurements
can be averaged per analysis cycle for an even greater
signal-to-noise, lower detection limit, and higher
measurement resolution.

5 NANO TCD GAS SENSORS: EXAMPLES

Figure 7 shows examples of gas measurements with the
nanoTCD device. We measured methane (CH$_4$) in dry air
between and CO$_2$ in humid air (40% RH). Lower detection
limit was in the 50-100 ppm range at 25 °C for CH$_4$, with
background T correction of the baseline signal for drift, and
c. 400 ppm for CO$_2$, fully corrected for T, P and RH
variation. Gas concentration can be corrected for
temperature (T), atmospheric pressure (P) and relative
humidity (RH) changes via built-in algorithms. We have
demonstrated our MEMS sensor element for measurement
of CO$_2$ for indoor air quality and demand controlled
ventilation applications [9].

6 SUMMARY AND CONCLUSIONS

We have presented several examples of new, ultralow
power gas sensors. These new sensors are poised to fill
burgeoning demand for chemical and gas sensors that will
be realized in the move toward a trillion sensor universe
[10].

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