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Reducing Food Waste with a Tiny CMOS-MEMS Gas Sensor, Dubbed GMOS †

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Abstract: We present a tiny combustion-type gas sensor (named GMOS) fabricated using standard CMOS-SOI-MEMS technology. It is a low-cost thermal sensor with an embedded heater, catalytic layer, and suspended transistor as a sensing element. The sensor principle relies on a combustion reaction of the gas that takes place on the catalytic layer. The exothermic combustion leads to a sensor temperature increase, which modifies the transistor current-voltage characteristics. The GMOS is useful for detecting different gases, such as ethanol, acetone, and especially ethylene, as well as their mixtures. The sensor demonstrates an excellent sensitivity to ethylene of 40 mV/ppm and selective ethylene detection using nanoparticle catalytic layers of Pt as well as TiO_2. Along with its low energy consumption, GMOS is a promising technology for low-cost ethylene detection systems at different stages in the food supply chain, and it may help reduce global fruit and vegetable loss and waste.

Keywords: Gas Sensor, CMOS, Pt nanoparticle, Ethylene, Selective gas detection

1. Introduction

Global food loss is one of the most urgent issues for the international community today. Waste and loss of fruits and vegetables may reach up to 50% of the initial production quantity [1]. Besides natural waste, lost food also represents the waste in resources for food production, such as water and energy, that leads to unnecessary CO_2 emissions. The immediate question that arises is, what can be done to reduce such high food losses? A possible solution is by monitoring the food storage environment. Fruits and vegetables produce ethylene gas during the ripening process; therefore, monitoring the ethylene level allows us to determine whether food is edible or ready for marketing before it is spoiled. This seems like an easy solution, but the problem lies in the low concentration of ethylene that needs to be monitored (0.05–10 ppm). To date, ethylene has been detected mostly by large, expensive, and non-selective detection systems.

The general trend for future gas sensors is towards smaller, cheaper, sensitive, selective, reliable, and low-power consuming sensors [2]. The prime gas sensor technologies are electrochemical, metal oxide semiconductor (MOX), calorimetric, and nondispersive infrared (NDIR) sensors. Each technology has its advantages and disadvantages, but the drawback that these technologies have in common is poor selectivity. The existing sensors are not fulfilling all of the requirements, which makes it important to develop new sensors, especially for ethylene, that can meet these demands.

We developed a sensor that meets all of the demands in one miniature solution. It is named GMOS, and was presented in [33–5] and is shown in Figure 1. GMOS is based on a thermal sensor

(named TMOS) that was invented by our group and has been studied over the past decade [6-11]. The TMOS sensing element is a suspended micromachined MOSFET transistor operating in the subthreshold, which was fabricated in CMOS-SOI technology and released with the MEMS backend process. The transistor has inherent gain, and therefore has high sensitivity in terms of the temperature coefficient of voltage, $TCV = \left(dV/dT\right)/V$, which leads to a low-cost, highly sensitive thermal sensor low power consumption. The advantages of TMOS were applied to GMOS for the fabrication of a high-performance thermal gas sensor.

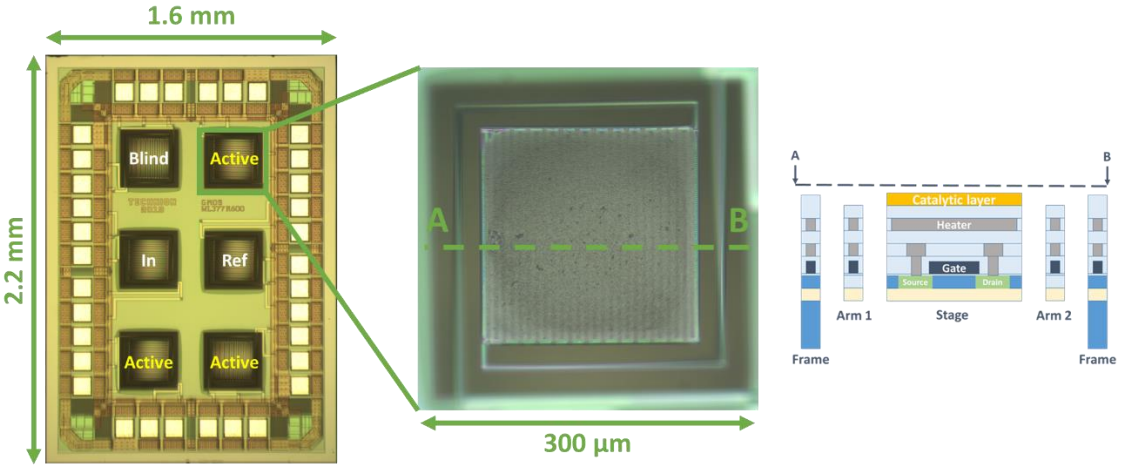


Figure 1. GMOS sensor die with six pixels: Two serve as sensor operation controls (pixels "In" and "Ref"), "Blind" is the reference pixel for differential measurement, and there are three "Active" pixels with catalysts for multi-gas detection. The readout circuitry is reported in [3].

2. Materials and Methods

2.1. GMOS Operating Principle

GMOS uses an embedded tungsten heating element to raise the temperature of the catalytic layer to the ignition temperature of the analyte gas. Due to the chemical oxidation of the gas on the catalytic layer surface, the heat of the reaction is released and increases the temperature of the whole sensor pixel including the sensing transistor. The transistor temperature increase modifies its current-voltage characteristics indicating the gas presence. The gas measurement is performed in a differential manner; thus, the detected signal is directly proportional to the temperature increase caused by the chemical reaction.

The key feature of GMOS is its selectivity. Unlike other miniature commercial gas sensors, GMOS uses an inherent property to detect gases in a selective way. The selectivity term is the ignition temperature, denoted T^*. This property is specific for a combination of analyte gas and catalytic material. Detecting gases at their ignition temperatures makes it possible to detect gases in mixtures with high precision. The detailed GMOS performance model is described in [5].

2.2. Experimental Setup

The experimental setup included a 6 L sealed gas chamber containing a battery-powered evaluation board with a GMOS sensor. The analyte gas was introduced through the inlet in gaseous form or using a liquid drop. In the latter case, the measurement was carried out after the drop's evaporation and the concentration was calculated using the ideal gas law equation. This setup was used for ethanol and acetone sensing studies.

For ethylene measurements, gas cylinders with a calibrated concentration of 10 and 100 ppm were purchased from Gasco (Oldsmar, USA) [12]. Ethylene gas flows from the cylinder at a constant flow rate of 0.5 slm and enters a small gas chamber with a volume of 20 mL. This chamber was mounted above the GMOS sensor and was open from the bottom side. Using that scheme, the

pressure difference was assumed to be negligible and the concentration near the sensor was assumed to be approximately equal to the concentration in the cylinder.

2.3. Catalytic Layers

Three kinds of catalytic layers were tested in this study: Pt deposited by sputtering; and Pt and TiO_2 nanoparticle layers. The sputtered Pt catalyst of 2000 Å was deposited on a 30 Å thick Ti adhesion layer. A Pt nanoparticle catalytic layer was deposited using a 20 wt % Pt ink purchased from Fraunhofer Inst (Dresden, Germany) [13]. A TiO_2 nanoparticle catalytic layer was deposited using a 20 wt % TiO_2 dispersion prepared by dissolving 13 nm TiO_2 powder in DI water and sonification for 30 minutes.

3. Results and Discussion

3.1. Multi-gas Sensing

The methodology of multi-gas sensing is demonstrated for the example of ethanol and acetone mixture. With the Pt sputtered catalyst, the two analytes have different ignition temperatures. Therefore, it is possible to define low and high working temperatures around the ignition temperature of each gas, as shown in Figure 2. At a low working temperature, only one gas can react, and its concentration can be obtained. Once detected at the low temperature, the signal of the first gas can be estimated for the high working temperature using a theoretical or experimental calibration curve for each gas, as shown in Figure 2a,b. In the second step, the signal is measured at a high working temperature. The observed signal is compared to the estimated one for the first gas. If the observed signal is higher than the estimated one, the difference is proportional to the signal of the second gas.

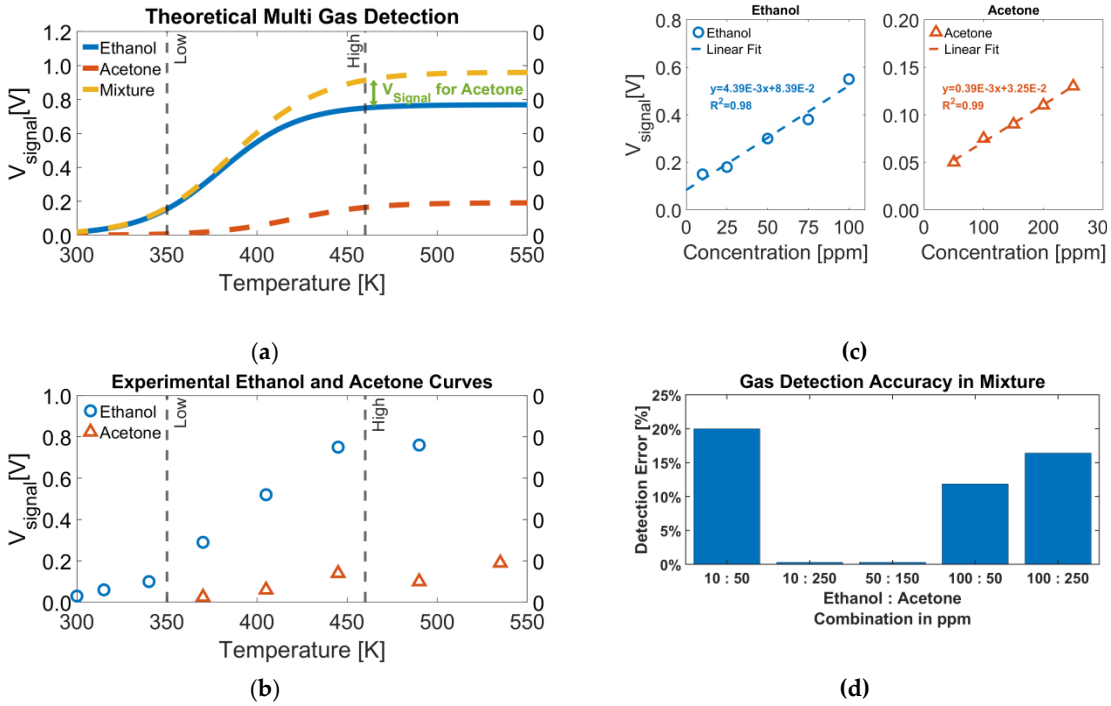


Figure 2. Multi-gas detection using two temperatures method. (a) Theoretical and (b) measured signal curves are shown for 100 ppm of ethanol and acetone as a function of pixel temperature on Pt sputtered layer. The right vertical axis shows the calculated pixel temperature increase due to the chemical reaction. (c) Voltage response to ethanol and acetone at high working temperature versus gas concentration; (d) detection accuracy in gas mixture relative to calibrated values of ethanol and acetone, in terms of detection error.

To demonstrate multi-gas sensing, a sensor response calibration for different ethanol and acetone concentrations was conducted at the high working temperature, as shown in Figure 2c. The calibration curves exhibit the excellent signal linearity and from the slope we can derive the chemical sensitivity of 4.4 and 0.4 mV/ppm for ethanol and acetone, respectively. A high sensitivity was achieved for ethanol gas but it was relatively low for acetone, which is the limiting condition in this experiment.

The concentration range for multi-gas detection was defined from 10 to 100 ppm and from 50 to 250 ppm for ethanol and acetone, respectively. To check the whole concentration window, we performed the gas detection on the concentration corners and in the middle (i.e. the ethanol:acetone mixture concentrations were 10:50, 10:250, 50:150, 100:50, and 100:250 ppm).

The detection accuracy is described in terms of detection error, $Error = \left(V_{Mix} / (V_{Ethanol} + V_{Acetone})\right) \times 100\%$, where V_{Mix} is the sensor signal observed in the gas mixture, and $V_{Ethanol}$ and $V_{Acetone}$ are the signals for ethanol and acetone according to the calibration curves in Figure 2c. The tested detection error was in the range of 0–20%, showing good detection accuracy. It will be shown that this methodology is applicable for ethylene in mixtures with other gases.

3.3. Selective Ethylene Detection

The benefits of ethylene monitoring in the supply chain are clear, as it could decrease food waste. The major requirements for new ethylene sensors are sensitivity, low cost, and selectivity. The main challenge is to obtain reasonable selectivity to ethylene for a reliable gas detection. GMOS is a sensitive sensor fabricated using low-cost technologies. Here, we will deal with the selectivity issue. GMOS is a chemical sensor and the oxidation reaction occurs on the catalytic plate. Therefore, the main approach is to find an appropriate catalytic material that can be selective to ethylene.

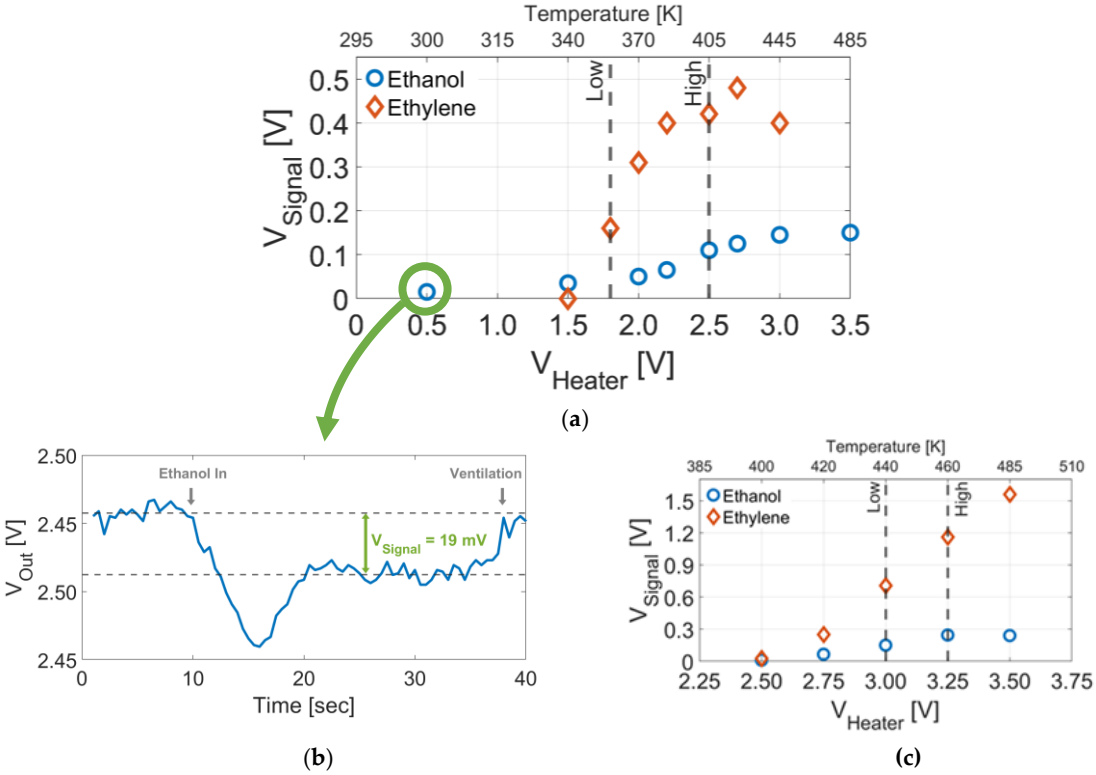


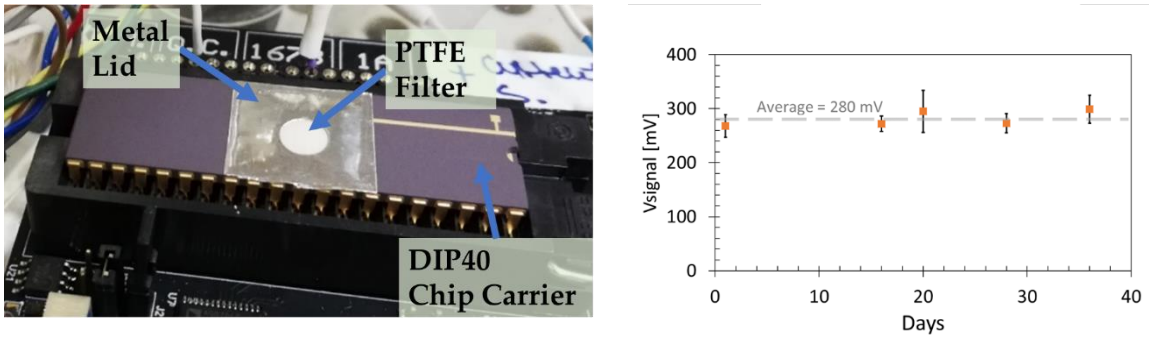
Figure 3. (a) Ethanol and ethylene signals as a function of heater voltage and pixel temperature for Pt nanoparticle catalytic layer when concentration is 10 ppm for both gases; upper scale denotes the average pixel temperature. (b) Ethanol signal at low pixel temperature where ethylene is not detected. (c) Ethanol and ethylene signal as a function of applied heater voltage for TiO_2 catalytic layer and gas concentrations of 100 ppm.

Noble metals, such as Pt and Pd, are known as ethylene oxidation catalysts [14]. Therefore, we started testing the GMOS response to ethylene with a Pt nanoparticle catalyst. The sensor response as a function of heater voltage is shown in Figure 3a. The sensitivities at ignition temperature (T^*) are about 30 mV/ppm and 8 mV/ppm for ethylene and ethanol, respectively. The maximum sensitivity reaches up to 40–45 mV/ppm, showing great potential for the detection of low ethylene concentrations. The ignition temperatures for ethylene and ethanol are close but not the same, which means it is possible to define high and low working temperatures for selective multi-gas detection, as shown in Figure 3a. Moreover, there is an interesting observation at very low heating temperatures (below 50 °C): There is a clear signal to ethanol, as can be seen in Figure 3b. At these temperatures, there is no signal for ethylene. Despite it being problematic to determine the exact concentration of ethanol at low temperatures, it still enables the detection of ethanol in the gas mixture or confirms its absence.

The other attempt to reach higher selectivity was using the TiO_2 catalyst, which should be more selective to ethylene [15]. The signal for ethylene and ethanol as a function of heater voltage is shown in Figure 3c. The sensitivity at ignition temperature is about 12 mV/ppm and 1.5 mV/ppm for ethylene and ethanol, respectively. The TiO_2 catalyst provides even better selectivity to ethylene than the Pt nanoparticle catalyst. The ignition temperatures are slightly different on the TiO_2 catalytic layer; therefore, selective detection is possible using the low and high temperatures method shown in Section 3.1.

3.4. Reliability

Long term stability is one of the most important factors for gas sensors, as the activity of the catalytic layer degrades over time. To postpone this degradation, the GMOS sensor is packaged with a metal lid and PTFE filter to prevent contamination of the catalytic surface (Figure 4a). In addition, the sensor was pre-heated for 30 minutes prior to the first use to clean the catalyst surface from organic contamination for best sensitivity performance. To keep the surface clean for a long time, a thermal refresh lasting a few seconds was performed before each measurement. Using these procedures, the sensor response to 100 ppm ethanol was tested over several weeks, as shown in Figure 4b, while between measurements the sensor was stored in ambient air.



(a) **(b)**

Figure 4. The sensor signal stability performed on a packaged GMOS sensor with a metal lid and PTFE filter (a) for five weeks of the experiment (b).

The signal remained stable for the five weeks of experiment with a variation that was within the standard deviation from the average signal. This shows that the applied procedures maintain sensor performance at the same level and prevent sensitivity degradation.

4. Conclusions

In this paper, we introduced the novel miniature gas sensor, GMOS. It has inherent benefits over prevalent commercial gas sensors, as it combines the main set of requirements into one sensor. It is miniature, cheap, requires low-power, sensitive, selective, and reliable. The multi-gas detection was shown for ethanol-acetone and ethylene-ethanol mixtures. High sensitivity and selectivity for

ethylene gas was obtained on Pt nanoparticle and TiO_2 catalysts. Together with good signal stability, this makes GMOS a leading candidate for future ethylene sensing applications to the control and monitoring of food supply chains which may reduce global fruit and vegetable loss and waste.

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