Temperature-Programmed Gas-Sensing With Microhotplates: an Opportunity to Enhance Microelectronic Gas Sensor Metrology

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Abstract. It is only recently that the ITRS (International Technical Roadmap for Semiconductors) has identified functional diversification through heterogeneous integration as a key enabler of future industry growth. This paper describes a powerful temperature-programmed gas-sensing technique that has the potential to convert low-cost, integrated, microhotplate-based non-selective, metal-oxide gas sensors into stable, sensitive, and highly selective gas-sensor systems. The paper also points out the importance of heterogeneous integration and temperature sensor stability to support this measurement technique.

Keywords: MEMS, Microhotplate, Gas sensor, Temperature programming, More than Moore, Heterogeneous integration, Functional diversification.
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INTRODUCTION

Progress in Moore's Law scaling (More Moore) has been the single driver for the primary growth and impact of the semiconductor industry since the invention of planar silicon technology. It is only within the last few years that the ITRS (International Technology Roadmap for Semiconductor) specifically identified progress in functional diversification (More than Moore) as being of equal importance to the continued growth of the industry. According to the ITRS, functional diversification involves miniaturizing and integrating passive, analog, and RF devices, sensors, actuators, and biochips with logic and memory in ever more powerful high-value systems. Cell phones provide a current example, and low-cost, high-performance gas sensors provide a future opportunity.

Temperature-programmed operations of arrays of metal-oxide semiconductor sensing-films [1] located on microhotplates have the potential to function as low-cost high-performance components that can be integrated with logic and memory to yield high-value gas-sensor systems in accordance with the "More than Moore" paradigm. For temperature-programmed gas-sensing to be viable, the microhotplate temperature must be accurately measured. Also because metal-oxide semiconductor gas sensors operate at elevated temperatures and their response is highly temperature dependent, such gas sensors need a robust temperature sensor whose temperature calibration must not drift more than a few degrees Celsius over periods of years.

The remainder of this paper will briefly discuss the potential benefits of integrated gas-sensor systems, the advantages of microhotplates as gas-sensor platforms, the power of temperature-programmed operation of metal-oxide gas sensors, and the heterogeneous integration of this type of sensor with control and measurement interface circuits and digital signal processing (DSP) algorithms.

WHO WANTS GAS SENSORS

Humans have a very poorly developed sense of smell compared to many other animals like dogs. For instance, when a person goes out into his yard on a spring morning, he might marvel at the colors of the newly opened flowers while his dog roams around the yard sniffing here and there. The dog is much less likely to be interested in the flowers and much more

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likely to be interested in the fact that some raccoons visited the yard and the pregnant deer gave birth last night. All of this information is available to the dog through its sense of smell.

Potential applications of so-called artificial noses are legion. But most of these applications require a level of performance per dollar that far exceeds the current state of the art. On the other hand, if sufficiently powerful systems were available at a suitably low cost, it could be beneficial to have a gas sensor in most enclosures.

Besides the more obvious uses that are already supported by commercial markets, such as detection of hazardous gases in industrial processes, these gas sensors could tell you that you have mice in your basement and a rotting potato in your pantry, that your new rug is slowly poisoning you, that your dinner has just reached the peak of culinary perfection, and that you should see a doctor soon because your breath indicates the possible onset of diabetes.

GAS SPECIES SELECTIVITY

Selectivity characterizes the ability of a gas sensor to identify different gases, and sensitivity quantifies the minimum concentration of a particular gas that the gas sensor can detect.

The most straightforward approach to selectivity is to use different gas sensors that respond to only one chemical species. The disadvantage of this approach is that it requires as many different gas sensors as there are gas species of interest in any given application. Therefore, it is practical only for applications where the number of target gases is small. A good example is monitoring an industrial process for leaks or accidental accumulations of the toxic gases that are used in that process.

Another approach to selectivity is to use a number of non-selective gas sensors that are non-selective in different ways. A thin film of tin oxide at an elevated temperature is a good example of a non-selective gas sensor [2]. In normal air, the electrical resistance of the film decreases when a combustible gas like methane or the vapor of ethanol (ethyl alcohol) is added to the air. But with steady-state operation of a single tin-oxide gas sensor it is not possible to determine either what combustible gas is present or how much is present just from the change in the resistance of the tin-oxide film. The conventional solution to this problem is to build a gas sensor consisting of an array of gas sensors with different thin films that are non-selective in different ways. For instance, different metal-oxide films such as tin oxide and zinc oxide can be deposited on different microhotplates or the same metal-oxide film can be deposited on different microhotplates in different ways to produce different gas-sensing properties [3-5]. This approach to selectivity, which nature uses for color vision, is quite powerful. For instance, if you have normal color vision then you can distinguish about 11,000 different colors with only the three nonselective visible-radiation photon sensors in your eyes. This approach to selectivity is based entirely upon the steady-state response of the sensors in the array. However, if it is possible to heat and cool the gas-sensor film on millisecond time scales, it is possible to use an even more powerful approach to selectivity that is called temperature-programmed gas sensing, and it is the small size of the microhotplate that enables the required millisecond heating and cooling.

MICROHOTPLATES

In its simplest embodiment, a microhotplate [6] consists of a membrane that contains a heater element suspended over an etch pit in a supporting substrate. For example, it is possible to use any of a number of standard commercial CMOS foundry processes to fabricate an integrated circuit (IC) chip that contains a precursor for a microhotplate on a silicon substrate. It is then possible to convert the microhotplate precursor into a functional microhotplate by carrying out further processing steps on the IC chip as illustrated in Fig. 1. In this case, the membrane is the interlayer dielectric stack available in the CMOS process, and the heater element is made from the polysilicon gate layer that is also available in a standard CMOS process [7].

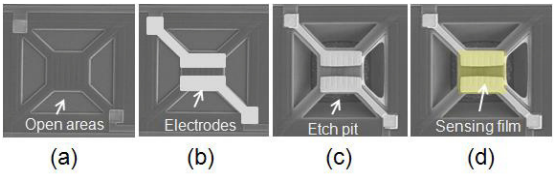

FIGURE 1. Steps for converting a microhotplate precursor to a functional gas-sensor.

Open areas in the interlayer dielectric expose the silicon substrate around the precursor as shown in Fig 1a. Usually these open areas are created in separate post-CMOS process steps.

If the microhotplate will be used as a platform for a conductance-type gas sensor, sensor-film electrodes will be formed on the microhotplate as illustrated in Fig. 1b. These electrodes are usually deposited with the same photolithographic processes that are used to fabricate CMOS ICs, but the metal films that are used for the electrodes are unlikely to be available from a standard CMOS processes.

The third step thermally isolates the microhotplate from the underlying substrate. This step is typically carried out with an isotropic etchant such as xenon difluoride or with an anisotropic etchant such as tetramethylammonium hydroxide. In either case, the etchant undercuts the precursor to create a functional microhotplate suspended over an etch pit as illustrated in Fig. 1c.

The final step is the deposition of the gas-sensing film. This is usually accomplished by decomposing a metal-organic compound on a hot surface to leave a metal-oxide film on that surface as illustrated in Fig. 1d. In most applications, the entire device has to be heated, and the metal-oxide film is deposited on all exposed surfaces of the entire device. However, in the case of an array of microhotplates, each microhotplate can be heated independently so that a different mixture of metal-organic gases can be used to deposit a different metal oxide on each microhotplate [3-5].

The unique attributes of microhotplates that make them particularly useful in certain applications include very small size, high thermal efficiency, and a small thermal time constant. In fact, it is the small thermal time constant that enables temperature-programmed operation, which was already mentioned in this paper and provides tunable selectivity to an otherwise non-selective gas sensor.

TEMPERATURE-PROGRAMMED GAS SENSING

A temperature program consists of a sequence of microhotplate temperatures to which the microhotplate is heated. For instance, a typical temperature sequence is illustrated at the bottom of Fig. 2 [8], but the actual temperature pulse sequence was actually much denser consisting of ten 100 ms pulses separated by 100 ms at each of eight temperatures ranging from 20 °C to 370 °C with 50 °C temperature increments.

Figure 2 plots the response of a microhotplate-based palladium-activated, tin-oxide gas sensor to this temperature program when exposed to different air samples that were saturated with vapors of acetone formaldehyde, methanol, or ethanol. Notice that the response to the two alcohols (methanol and ethanol) is very similar but quite different from the response to the aldehyde (formaldehyde) and the ketone (acetone). Suppose that a gas sample containing a mixture of methanol and ethanol has been measured with the same gas sensor used to produce the data in Fig. 2 and that it gave a response intermediate between the curves shown in Fig. 2. It might be difficult to accurately determine the composition of the mixture of methanol and ethanol because there is not very much difference between the methanol and ethanol curves in Fig. 2. The solution to this problem is to switch to a different temperature program that was optimized to distinguish among different alcohols rather than to distinguish alcohols from other chemical species as illustrated in Fig. 3 [9]. The top panel of Fig. 3 shows a different temperature program from the one that was described at the beginning of this section and that was used to obtain the data shown in Fig. 2. This temperature program was found by a neural network analysis that was designed to maximize the differences between the responses to methanol and ethanol. Note that the period increased from 17 s to 21 s, the temperature range was reduced from 350 °C to 50 °C, and the shape of the sequence was drastically altered.

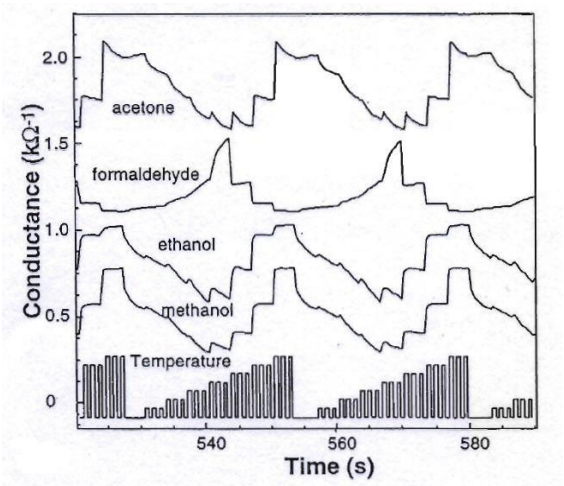

FIGURE 2. Shows response curves from a microhotplate-based, palladium-doped, tin-oxide gas sensor when exposed to different gas species with temperature-programmed sensing.

When the same gas sensor whose response is shown in Fig. 2 is operated with the temperature program shown in the top panel of Fig. 3, separate exposure to air saturated with methanol and ethanol produce the responses shown in bottom panel of Fig. 3. Notice that these responses are almost the opposite of each other. Thus, it will be possible to determine the relative concentrations of methanol and ethanol in a methanol-ethanol mixture more accurately with the temperature program used to generate Fig 3 than with that used to generate Fig. 2.

The combination of temperature programming with an array of microhotplate-based gas sensors that have different non-selective gas-sensor films is even more powerful. For instance, references [3-4] describe the use of a sixteen element array with a simple, linear 5 °C per second temperature-ramp program and film-conductivity measurements taken every 1 °C from 150 °C to 500 °C. This procedure produces 16 x 350 = 5600 features, which are then used in a hierarchal

recognition procedure to distinguish between different chemically similar classes of compounds based on training on a small number of representatives of each class.

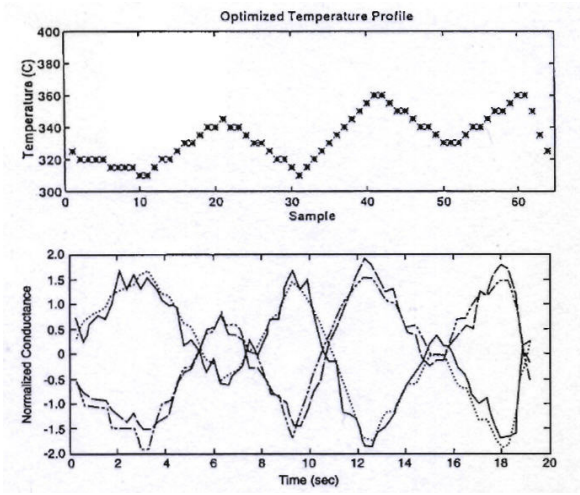

FIGURE 3. (top) Temperature program sequence. (bottom) Methanol and ethanol response to temperature program.

HETEROGENEOUS INTEGRATION

To take full advantage of temperature program sensing and to make this powerful technique a practical reality for low-cost gas-sensor systems, integration of control and measurement circuits with microhotplate gas sensors appears to be essential [7,10-11]. Not only will heterogeneous integration of microhotplate-based gas-sensor arrays with control and signal processing electronics reduce the cost of this type of gas sensor but it also has the potential to improve the performance because tight integration reduces noise pickup and other sources of irreproducibility.

However, it is not yet clear what the optimum level of integration is. System-On-a-Chip (SOC) solutions provide the highest level of integration but are not currently the most practical solutions for many applications that require heterogeneous integration. In many of these applications, such as cell phones, System-In-a-Package (SIP) solutions have been able to deliver most of the performance advantages of SOCs while avoiding many of the as-yet-unsolved problems.

It is beyond the scope of this paper to examine the trade-offs between SOCs and SIPs, but Fig. 4 typifies a design philosophy that is compatible with both. This figure shows the layout of a gas-sensor die comprised of an array of four microhotplate-based gas-sensors integrated together with decoders, an analog-to-digital convertor, amplifiers, and bonding pads, all of which were fabricated on a 2 mm by 2 mm integrated circuit die in 1.5 µm standard CMOS process [11].

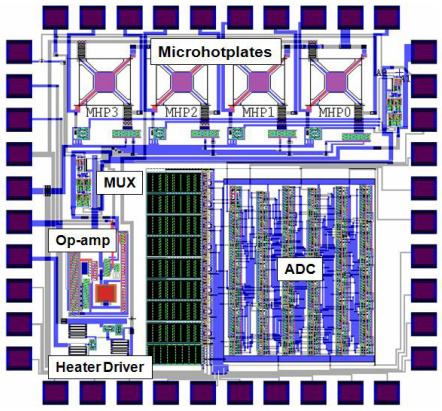

FIGURE 4. A layout of a 2 mm x 2 mm gas sensor system chip showing four microhotplates, an 8-bit ADC, an op-amp, a MUX, and a heater driver.

With this approach, all of the analog-signal processing and control electronics as well as the microhotplates are encapsulated in a digital interface for integration with a microprocessor to form a gas-sensor system. This die might be mounted on top of a microprocessor die and wire bonded to form an SIP. Alternatively, the same layout with the bonding pads removed could be combined with the layout for a microprocessor to form an SOC.

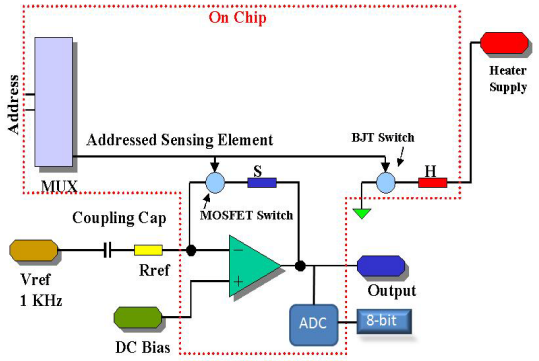

FIGURE 5. Schematic diagram of gas-sensor system of the gas-sensor chip layout shown in Fig. 4. Only the circuits associated with one of the four microhotplate heaters are shown.

Figure 5 is the schematic diagram of the gas-sensor system shown in Fig. 4, depicting its input/output ports. In this gas-sensor system only one gas-sensing element is active at any given time and only the addressed sensing element is shown in the figure.

A 1 kHz sinusoid is used as a reference signal to the inverting input of the operational amplifier. Capacitive coupling of the reference sinusoidal signals

prevents DC offset and drift problems in the measurements, thus insuring symmetric clipping for maximum dynamic range. A user-selectable DC bias to the non-inverting amplifier input can be adjusted to maximize the dynamic range.

The IC die whose layout is shown in Fig. 4 was developed as a platform to identify and investigate potential needs for metrology and standards to support heterogeneous integration of microhotplate-based gas-sensor systems. One problem identified in this way is the requirement for improved long-term repeatability temperature-measurement stability.

In this connection, [12] shows two independent temperature-measurement techniques that agreed with each other to within plus or minus 2 °C over a period of three months exposure to temperatures in the vicinity of 400 °C following a single calibration at the beginning of the three-month period. One of these measurement techniques is based on an integrated Platinum/Rhodium thermocouple. The other is based on the thermal efficiency of the microhotplate. These can be used together or either one in combination with an integrated thin-film resistive platinum-temperature sensor to support temperature-sensor built-in-self-test.

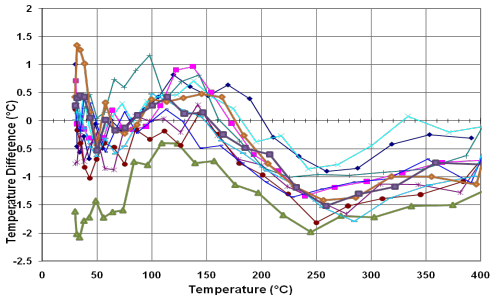

FIGURE 6. Differences between the microhotplate temperatures measured with platinum-rhodium thermocouple and microhotplate thermal resistance at 11 different times during a period of 3 months.

CONCLUSION

It is clear that a temperature-programmed array of microhotplate-based gas sensors has the potential to be a very powerful gas-sensor system that exemplifies the "More than Moore" paradigm. It is also clear that a number of technical problems remain to be solved before this technology can live up to its potential and many of these involve metrology and measurement science that fall within the mission of the NIST Semiconductor Electronics Division.

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