Chapter 2 History of Chemical Sensing

Classical solutions to chemical sensing tasks have been dominated by complex, expensive laboratory methods such as gas chromatography and ion-mobility spectroscopy. Although these methods are accurate for detecting chemical concentration and in discriminating among chemicals, their cost is often prohibitive for many low-end, chemical sensing applications ranging from residential sensing of toxic chemicals to the detection of seafood freshness and breath alcohol analysis. To lower the cost of chemical sensing systems sufficiently to compete in these low-cost markets, a new approach to chemical sensing needs to be adopted.

In order to address the needs for chemical sensing systems in consumer and other low-end markets, it has been useful to use miniaturization techniques that perhaps sacrifice some of the accuracy of laboratory methods for lower cost, faster response times and greater accessibility. Since the early 1970's, the microelectronic chemical sensor has been investigated as this low-cost, miniaturized alternative to laboratory chemical sensing methods. However, the miniature chemical sensor has been plagued by problems with:

- Reproducibility: inconsistent responses to the same chemical over time.
- Selectivity: difficulty in discriminating among chemicals.
- Sensitivity: difficulty in detecting low concentrations of particular chemicals.
- Stability: difficulty in detecting chemicals of interest across changes in ambient conditions.
- Response time: typically on the order of tens of seconds to minutes

Chemical sensing systems that overcome some or all of these problems have had difficulty in keeping system cost down at a manageable level for the corresponding market for particular sensing applications. However, some progress has been made in the research community since the 1970's in addressing this delicate balance between cost and robustness of viable chemical sensing systems. There are three general tasks of interest in these systems: concentration detection, chemical discrimination, and response time optimization. Most microelectronic chemical sensors are able to detect concentration reasonably well at medium to high concentrations. As a result, this

research has focussed on the more complicated issues of discriminating among chemicals and minimizing response time.

In this chapter, an overview of the chemical sensing problem is presented in order to provide the reader with a more detailed understanding of the problems addressed in this research. This research is related to efforts currently ongoing in the research community as well as to the biological basis discussed in the previous chapter. The chapter concludes with a detailed description of two of the most common chemical sensor technologies, the thin-film sensor and the ChemFET; these two technologies are best suited for integration with the signal processing architectures developed in this research. The signal processing architectures implemented in this research are designed for implementation into one of the frameworks discussed in detail in Chapter 7.

2.1 History of the Individual Chemical Sensor

Since the 1970's, the microelectronic chemical sensor has been explored as a low-cost alternative to laboratory chemical sensing methods. Many of the microelectronic sensor technologies are based simply on conductivity changes in a material in response to chemicals in the environment. The simplest of these conductivity-based sensors, the thin-film sensor, was first introduced into the research community in the early 1970's. The thin-film sensor (Figure 2.1) is simply a film of chemically sensitive material, such as tin oxide [9] or polypyrrole [10] whose conductivity changes in response to reducing chemicals in the sensing environment.

The metal-oxide, thin-film sensors are the only miniaturized chemical sensors that have had significant impact in commercial markets. For example, tin oxide (SnO_2) and iron oxide (Fe_2O_3) [11] have frequently been used to detect hydrocarbons and combustible gases in a variety of applications. By far, the most popular of these sensors has been the Taguchi-type sensor, manufactured by Figaro Engineering in Japan; these sensors are made up of primarily tin oxide modified with various catalysts and additives to detect particular hazardous gases such as carbon monoxide and methane [12]. Because of their commercial availability, these sensors, in discrete form, have been used to evaluate the feasibility of this research.



This sensor consists simply of a thin-film of chemically sensitive material whose conductivity changes in response to certain chemicals in the sensing environment. The thinness of the film is required, because these conductivity changes are primarily based on surface interactions and the surface must be a significant part of

the entire sensor in order to detect these changes. The output of the sensor may be read either as a current or as

Figure 2.1: Basic Structure of the Thin-Film Sensor

Perhaps the most important promise of these thin-film sensors for the development of viable chemical microsystems is their compatibility with standard integrated circuit fabrication processes. Metal oxides and conducting polymers can be deposited onto standard integrated circuit substrates often after circuits have already been fabricated on the same substrate. With current advances in micromachining technology available through prototyping services such as MOSIS [13] and MUMPs [14], it has become feasible to develop these sensors in conjunction with complex signal processing on single chips for research and development. Because of their suitability to integrated systems and to this research, the theory of thin-film sensors is discussed in greater detail at the end of this chapter.

a voltage.

Also, in the early 1970's, the ISFET was developed in the research community. An ISFET (Figure 2.2a) is simply a MOSFET without a gate. The oxide layer of the FET is replaced with an insulating, chemically sensitive membrane. Charges from sensitive chemicals accumulate on top of this insulating membrane and are amplified through the operation of the FET [15]. Although the amplification properties of the transistor in these devices seem very attractive for sensing chemicals, the vulnerability of the insulating membrane to environmental poisoning and subsequent transistor breakdown has prevented the ISFET from gaining popularity in commercial markets. Since the insulator layer provides no optical shielding from the surrounding FET device, light sensitivity has also proven to be a problem with these devices. As a result, the ChemFET (Figure 2.2b), although less selective and chemically sensitive than the ISFET, has demonstrated more potential for integration into practical chemical sensing applications. Unlike the ISFET, the ChemFET uses a standard oxide layer as the insulator and a chemically sensitive metal, such as palladium, as the gate [16]. The addition of the gate minimizes light sensitivity problems that are a problem in ISFETs. Likewise, potential poisoning of the oxide layer is minimized not only by the inherent physical barrier provided by the metal gate but also by the fact that the silicon dioxide is fairly resilient to environmental poisoning. Modifications and hybrids of the ChemFET and the ISFET such as the surface accessible FET or SAFET [17] (Figure 2.2c) and the Suspended Gate FET or SGFET [18] (Figure 2.2d) were also introduced into the research community in the 1970's; despite the enhanced selectivity and sensitivity of these devices over the ChemFET, however, they share the common flaw of a short lifetime due to the accelerated degradation of the partially or completely exposed oxide layer. Because of its relative low sensitivity to environmental degradation, the ChemFET is thought to be the most promising of the MOSFET-based chemical sensors in spite of its relatively low selectivity compared to other chemically sensitive FETS.

The ChemFET sensors are also well suited to monolithic integration onto standard integrated circuit substrates. Although fabrication of these devices on standard substrates is more complex and slightly less advanced than that of the thin film devices, the technology for integration is nevertheless currently available in the research community. For reasons of compatibility, then, the theory of MOSFET-based chemical sensors is also discussed in greater detail at the end of this chapter so that the reader may better understand how ChemFETs may be structured in complete arrays and systems for chemical signal processing.

The MOS-based and conductivity based devices described above belong to the single largest class of microelectronic chemical sensors: those based on a single stage of transduction between chemical input and electrical output signal. Significant improvements in the sensor response times are attained as a result of this single level of transduction. Furthermore, the cost of implementing and manufacturing systems that use single transduction stage devices for chemical sensing is minimized by the fact that standard microfabrication techniques are frequently sufficient to produce many of the MOS-based and conductivity based sensors.



accessible FET), and (d) SGFET (suspended gate FET). All devices except the ChemFET suffer long term stability problems caused by the exposure of the insulator layer to damaging effects in the sensing environment.

Although the ChemFET and thin-film sensors are undoubtedly the most popular of the single transduction-stage chemical sensors, a variety of other chemical sensors have also been explored in the last two decades for accomplishing chemical analysis tasks. Chemically sensitive MOS capacitors are similar to ChemFETs; however, since they lack the source and drain of the Chem-FET, their capacitive output is difficult to capture and process for chemical analysis. Chemically sensitive Schottky barrier diodes contain a chemically sensitive metal as the top layer of the diode [19]; the diode barrier height alters in the presence of a reducing chemical; however, as in the case of the MOS capacitor, this change in barrier height is difficult to measure in a reliable and reproducible manner. The solid electrolyte has also shown potential for improved performance over ChemFET and thin-film sensors, since many of the electrolytes available that are chemically sensi-

tive have an ionic sensitivity that is highly selective to particular chemicals [20][21]. However, fabrication difficulties involved in bulk micromachining and establishing a reference electrode for these devices have prevented most electrolyte-based devices from becoming commercially viable.

Aside from these devices that translate chemical concentration directly to an electrical signal, multiple stage transduction devices have demonstrated use for chemical sensing applications. The thermal sensor uses a thermistor or similar temperature sensor to measure the heat generated by reactions between particular chemicals and the chemically selective layer coating the temperature sensors. However, the low efficiency of these devices in capturing reaction heat limits their suitability for the low concentration thresholds required of many chemical sensing applications. The mass sensors, on the other hand, suffer from the opposite problem. Based on sensing the added mass of a chemical reacting with the sensor surface, these devices are extremely sensitive, making them also very noisy and inherently vulnerable to interference. The piezoelectric sensors which sense the added stress or force of an additional mass on the sensor surface have very broad selectivity and consequently, poor discrimination capability. Another class of mass sensors, the surface acoustic wave devices have improved selectivity over their piezoelectric counterparts and can often be made using standard IC fabrication techniques. In an SAW sensor, a chemical reacts with a chemically selective layer on the sensor surface, causing a frequency, phase, or amplitude shift in the acoustic wave travelling across the device; the wave itself can be generated via piezoelectric behavior, acoustic coupling, or similar means. Despite their improved selectivity, however, the SAW sensors often experience prohibitively long response times (on the order of 20 minutes) for many chemical sensing applications. Finally, the optical sensor has two key advantages over all other types of chemical sensors. The light absorption of a particular chemical is often very specific to that chemical, giving the optical sensors very precise selectivity; the added advantage of this sensing technique is that in optical sensing, the chemical sensing environment is not required to interact physically with the sensor. This characteristic makes optical sensors well suited to remote sensing and applications where electricity in the sensing environment can be hazardous. However, optical sensors frequently require the use of mirrors, beam splitters, and other specialized optics that tend to make these systems higher cost than their solid-state counterparts [22]. Due to the importance of low-cost in addressing many of the common needs for chemical sensing systems, the focus of this research remains on the single-transduction stage devices as the best of the sensor technology choices currently available for these low low-cost systems. By far, these microelectronic sensors have the most compatibility with standard fabrication processes that inherently keep product development and unit costs low.

2.2 The Introduction of the Chemical Sensor Array

Overall, the individual chemical sensor has done quite well in detecting concentrations of particular chemicals. However, in sensing environments that are potentially visited by nuisance chemicals that are not of interest in a particular application, false concentration readings can often occur in response to these nuisance chemicals. These concentration errors, while nontrivial, are overshadowed by poor selectivity which is the primary problem associated with many microelectronic chemical sensors. Most sensors are inherently sensitive to a wide variety of chemicals. Tin oxide, for example, responds in a similar manner to all reducing chemicals, making discrimination among those chemicals difficult if not impossible in a single sensor. It is because of this problem with selectivity as well as other issues with reliability and reproducibility that the microelectronic chemical sensing technologies have been largely unable to bridge the gap between research and manufacturing since their initial development in the research community. These issues have prompted recent interest in arrays of chemical sensors; designed properly, these arrays, accompanied by appropriate signal processing techniques, have proven successful in solving discrimination problems previously intractable in individual sensor operation. Arrays of microelectronic chemical sensors first began to appear in the early 1980's and have advanced the state of microelectronic chemical sensing a great deal in the past decade.

A number of variables have proven useful for improving the discrimination capability of a group or array of chemical sensors. For example, external material filters have improved the resistance of chemical sensors to interference from nuisance chemicals in the sensing environment. Bott and Jones used this parameter on an array of six sensors by adding various oxidizing filters on sensor surfaces to distinguish among various combustible gases [23]. Similarly, Muller and Lange used four palladium MOS-based chemical sensors covered by zeolite filters to discriminate among various chemicals [24]. Meyer *et al* [25] employed various external membranes to enhance the selectivity of platinum electrodes to urea and ammonia for biological applications. Similar to the effect of filters, the addition of catalysts to chemically sensitive materials can also alter and narrow their selectivity in an array. Wang *et al* used palladium as a catalyst to enhance the discrimination capability of an array of metal-oxide sensors for analyzing mixtures of acetone and methanol [26]. Other modifications of sensor physical properties include varying grain size [27] in thin-film sensors during fabrication to improve the selectivity of the sensor array. By far, however, the most popular array variable for chemical sensing has been operating temperature. Operating temperature is not only an easily modified parameter; it also broadens selectivity and sensitivity of many sensors to a wide variety of chemicals [28]. The choice of array parameters is certainly important in establishing the overall effectiveness of the array in accomplishing a particular chemical discrimination task.

However, the effectiveness of a chemical sensing system for discriminating among chemicals is also highly dependent on the signal processing techniques used to process the array inputs provided by these sensors. In recent research efforts, signal processing has been implemented as part of complete chemical sensing systems in three major ways:

- Software-based signal processing requiring the use of a digital computer to train, calibrate, and analyze chemical sensory input.
- Hardware-based signal processing located external to the sensing plane to store training and calibration data and to detect chemical patterns for discrimination tasks.
- Hardware-based signal processing located on the sensing plane itself that is designed to amplify and extract important features of the sensory input.

By far, the most popular of the signal processing techniques used to process chemical sensor arrays has been the software-based solutions. In the early 1980's, statistical techniques were commonly employed to analyze sensor input for discriminating among chemicals. Ikegami and Kanyesau used standard statistical pattern determination techniques [29] to distinguish among reducing gases in an array of conductivity-based sensors made with various semiconducting oxides. Shurmer et al [30] used weighted fault-tolerant least squares techniques to discriminate among various alcohols in an array of tin oxide sensors, Similar efforts to improve the discrimination capabilities of microelectronic chemical sensor array have used discriminating function analysis and multivariate analysis of variance techniques [31] and principal cluster analysis [32]. More recently, however, artificial neural networks have enjoyed substantial popularity in software-based analysis of chemical sensor arrays. The popularity of artificial neural networks in these applications can be directly attributed to their resilience to interference from nuisance chemicals and to fluctuations in sensor performance caused by drift and humidity effects. The well-known back-propagation trained multi-layer perceptrons has been implemented successfully to distinguish among various alcohols [33][26], beers [34], food flavors [35], types of paper [36], and between ammonia and hydrogen [37], The less popular artificial neural networks that use unsupervised learning techniques such as the Kohonen Map have also been used to successfully distinguish between aromatic and spicy odors [38]; these unsupervised techniques have the additional advantage of accommodating drift and other long term effects better than their supervised counterparts since learning continues throughout the lifetime of the sensor array. Through artificial neural networks and other statistical

analysis techniques, software has provided flexible, easily modifiable modes for analyzing arrays of sensory output. However, while software-based solutions have proven invaluable in exploring and determining optimal methods for analyzing chemicals, they have all used a digital microcomputer or similarly complex hardware which is often cost-prohibitive for many common chemical sensing applications.

As a result, new effort has focussed on implementing effective chemical discrimination algorithms in hardware. Gardner *et al* developed a system that, although trained on a digital computer, operates from a series of custom PCB's that contain all the interface circuitry and signal conditioning for particular discrimination tasks [39]. While this system still requires software-based neural network training and operation, it is a first step in moving toward a stand-alone system for detecting the quality and maturation of beer in the manufacturing process. In another effort, Hines and Gardner develop a stand-alone artificial neural emulator for processing an array of tin oxide sensors that requires a digital computer only for the training of the neural networks [40]. Unfortunately, the use of custom PCB's and off chip components also increases the cost of the overall chemical analysis system. Much of the processing that is currently done off chip in hardware or software can be moved on-chip in appropriately chosen chemical sensor arrays and integration technologies. Alone, these single-chip systems can provide solutions to simple chemical signals for more complex processing to be performed off-chip.

Some work has been done in implementing conventional serial processing techniques on the same substrate as arrays of chemical sensors. For assessing purity in semiconductor fabrication processes, Najafi *et al* integrated a heater controller, AC and DC sensing units, and an 8-line front-end standard interface with platinum and titanium sensors [41]. The integrated array can detect oxygen at sub-ppm values even in the presence of the nuisance gas CF_4 . Similarly, Meyer *et al* integrated read-out amplifiers with an array of 400 platinum electrodes for biological, chemical sensing tasks [25]. Schoneberg *et al* resolved interference in sensor performance from drift by fabricating a reference MOS capacitor on chip with a chemically sensitive MOS capacitor and integrating switched capacitor circuitry with this sensor array in order to continuously eliminate the baseline from chemical sensor outputs [42]. The common thread underlying the efforts described above is the fact that they frequently process chemical sensor signals using generic, serial techniques. Although these circuits reside on the same substrate as the actual chemical sensors, they often are not an integral part of the sensor itself. On the other hand, the collective architectures

outlined in this research, are some of the first "smart" pixel approaches that specifically address chemical sensing issues.

Whatever the method of implementation, three major factors need to be considered in developing a complete chemical microsystem:

- Sensor Technology
- Type of signal processing
- Array architecture

The collective signal processing used in this research has already been explained and justified in the previous chapter. The choice of an array architecture is somewhat more complicated and is described in further detail in Chapter 3. In this chapter, the two most appropriate choices for monolithic integration with signal processing circuits, ChemFETs and thin-film sensors, are described in detail. An understanding of their operation is important to choosing an array architecture that maximizes the robustness and information available in an array of chemical sensors.

2.3 Thin-Film and MOSFET based Sensor Technologies

Primarily because of their compatibility with standard semiconductor fabrication processes, the thin-film chemical sensor and the related MOSFET-based chemical sensor appear to be the most promising for integration into complete, monolithic chemical sensing microsystems. The science governing the operation of these two types of sensors are discussed in greater detail here; an understanding of their basic operation is fundamental to determining a suitable array architecture and signal processing mode for solving a variety of chemical sensing problems. Solutions to the problems of integrating sensors and circuits onto the same substrate are also being addressed elsewhere in the research community and are discussed in further detail in Chapter 7.

2.3.1 Thin-Film Chemical Sensor Technologies

The sensing of reducing chemicals by a chemically sensitive thin film occurs primarily as a result of surface interactions. Consider a homopolar material such as silicon; although silicon is not usually considered chemically sensitive, it makes a good example for explaining other more chemically sensitive materials. In the bulk region, silicon shares an electron with each of four neighbors, an electrically insulating arrangement. At the surface, however, silicon does not have four neighbors; as a result, a solitary unpaired electron per silicon atom will exist at the surface, thereby creating a dangling bond. The dangling bond may either attract another electron from or be injected into the conduction band in the bulk of the silicon. Luring an electron from the bulk decreases the conductivity whereas injecting an electron into the bulk increases the conductivity. Other semiconductors, including most chemically sensitive metal-oxides are ionic rather than homopolar (covalent) as in silicon. At the surface of these semiconductors, the metal usually acts as a cation, accepting electrons from the semiconductor bulk while the oxide acts as an anion, donating electrons to the semiconductor bulk. In either case, homopolar or ionic, as electrons are donated to the bulk, a positive charge accumulates [43]. Whether the electrons migrate to or from the surface of the chemically sensitive film depends on the location of the surface energy bands relative to these in the bulk of the material. The relative location of these energy bands is affected by but not limited to the following factors:

- Exposure of different crystal faces at the surface
- Grain boundaries at the surface
- Dislocations
- Mixed phases
- Amorphous Regions
- Patches of oxides or other foreign phases

Most chemically sensitive films are n-type in nature and the surface band of energies is usually located within the forbidden gap of the material. In this situation, electrons are extracted from the bulk to the lesser energy bands at the surface, allowing a net negative charge to accumulate there. Oxygen in the ambient environment is then attracted to and bonds to the surface. When a reducing chemical becomes present in the sensing environment, it reacts with the oxygen, thereby removing it from the surface of the thin-film and reinjecting electrons into the bulk. This has the net effect of increasing the film's conductivity in the presence of reducing chemicals. Tin oxide has become the most popular chemically sensitive thin-film largely due to its long-term stability properties. Other thin films such as zinc oxide, titanium oxide and the polymer polypyrrole may be more selective or sensitive, but suffer from problems with drift and reproducibility [9][10].

The resistance of these chemically sensitive thin films is typically proportional to the concentration of a particular chemical in the environment according to the following relationship:

$$R = \frac{1}{G} = \alpha \log[C] \tag{2.1}$$

where *R* is the resistance of the thin film, *G* the conductivity, α a constant and [*C*] is the concentration of the chemical in the sensing environment [44]. The constant α can change with a number of factors; how it changes with parameters in an array of chemical sensors is important for understanding how to design such arrays.

The proportionality constant α can change in response to a number of operating conditions and physical properties of the component sensors in an array. For example, changes in grain size [27], the addition of catalysts [45], and the use of external particles filters [23] are well known to affect the sensitivity and discrimination capability of many microelectronic chemical sensors. Similarly, changes in operating conditions such as temperature affect sensor response sufficiently to support their use in heterogeneous arrays for chemical discrimination [28].

Of the parameters that may be chosen to lay out an array of chemical sensors, operating temperature is the most widely chosen because of its flexibility. Unlike physical properties which are usually set during fabrication, temperature may be varied at any time, during fabrication, off-line, or during regular operation of a sensor array. The response of a thin-film sensor varies for a particular chemical at different operating temperatures. These variable sensitivities over temperature may be used to obtain a unique signature for many different chemicals, thereby enhancing the selectivity of individual sensors without actually altering their physical properties.

2.3.2 MOSFET-based Chemical Sensor Technologies

As discussed previously, the ChemFET is the most practical and widely used of the MOSFETbased chemical sensor technologies due to its long-term stability and reproducibility relative to other sensors within this category. The ChemFET consists of a MOSFET whose gate polysilicon or metal has been replaced with a chemically sensitive metal or conductive material such as platinum or palladium. Chemicals in the sensing environment react with the gate, altering its work function and producing the following change in threshold voltage:

$$V_t = \Delta \phi_{m(max)} \left[\frac{k_1 [C]^{0.5}}{1 + k_1 [C]^{0.5}} \right] + k_2$$
(2.2)

where $\Delta \phi_{m(max)}$ is the total number of adsorption sites available to the chemical C, [C] is the concentration of chemical C, k_2 combines various MOSFET design and process dependent parameters and k_1 is an equilibrium rate constant combining adsorption and desorption of oxygen at the surface of these sensors and the reduction of O_2^- and O^- by the chemical C [19].

Obviously, the MOSFET structure used to make a ChemFET is compatible with standard MOS fabrication processes. ChemFET compatibility with integrated circuits is actually better than that for thin-film sensors since they can operate successfully at temperatures around 150° C where many metal-oxide, thin-film sensors must operate above 300° C. In either case, some thermal isolation or heat dissipation must be designed into these integrated systems to protect the on-board circuits from the excessive heat needed to maintain sensitivity in the chemical sensors themselves. The primary difference between the thin film sensors and the ChemFETs, however, is their failure mode. Thin film sensors fail gradually, poisoned by irreversible reactions with the sensing environment until their output reaches a saturated maximum that no longer responds to chemicals in the sensing environment. ChemFETs, however, usually fail when the gate oxide is shorted out or shunted by environmental poisoning generated by humidity or corrosive chemicals. As a result, the failure mode of a ChemFET is expressed as a saturated minimum or zero output as opposed to the maximum output generated by the failed, thin-film sensor. The effect of these broken sensors must be minimized or eliminated in an array, so that they do not cause failure of the entire system when broken.

Like the thin-film sensors, the sensitivity of the ChemFETS may be altered by varying physical properties of the chemically sensitive gate material through the inclusion of various additives or through the modification of such conditions as operating temperature [46][47][48][49].

In any case, the primary reasons for choosing the thin-film and ChemFET chemical sensor technologies are as follows, in order of priority:

- compatibility with standard semiconductor fabrication processes
- compatibility of operation with standard integrated circuits (CMOS)
- ease of prototyping in non-customized research environment
- availability of parameters for designing heterogeneous arrays of these sensors

Without compatibility with standard IC processes, chemical sensing microsystems are for many applications, impractical. Without ease of prototyping, it becomes difficult to combine research expertise for sensor fabrication and signal processing sufficiently to design and develop viable systems. Finally, without array flexibility, these sensors cannot gain the discrimination capability and sensitivity required for many sensing tasks. In the chapters that follow, discrimination tasks are addressed through the use of chemical sensor arrays while remaining within the constraints of standard microelectronic fabrication processes.