Chemical Microsensors

by C. C. Liu, P. J. Hesketh, and G. W. Hunter

The need for chemical sensor technology in applications such as industrial processing, aerospace, and security has increased in recent years. In practice, the sensing elements must be relatively small in size, robust, and should not require a large sensing sample volume.[1] Multiple sensing elements in a sensor array are often required to meet the needs of many applications. Further, a fully operating sensor system may be composed of not only the sensor elements but also supporting technology, such as integrated signal processing, power, communication, and packaging to form complete systems. Silicon-based processing techniques are increasingly being used to create chemical sensor microsystems to meet the needs of these applications.[2,3]

In this article we discuss silicon-based processing techniques (commonly referred to as microelectromechanical systems or MEMS technology) and their use in the fabrication of chemical sensing microsystems.[4] These processing techniques have enabled the fabrication of new sensor structures and sensor arrays with high capabilities but limited size, weight, and power consumption. We give examples here of the various types of sensor structures (platforms) that MEMS processing can enable and the wide range of chemical sensing capabilities that result from use of these platforms. Miniature gas chromatograph (GC) technology that complements and enhances the capabilities of the microsensors is discussed as an example of how MEMS processing can contribute to a complete chemical sensing microsystem. Given the space constraints, this article is not an exhaustive survey and does not cover such issues as power, communication, and packaging that go into a microsystem. Rather, this discussion is meant to illustrate the many possible tools provided by MEMS processing that are available when one is confronted with a chemical sensing problem. Each sensing technique has advantages and limitations. It is important to recognize the viability and applicability of each technique and to choose the best one to meet the application needs.

Silicon-Based Processing Applied to Chemical Sensors

Silicon-based microfabrication technologies provide the advantage of producing microsize structures in an identical, highly uniform, and geometrically well-defined manner.[2,4] Thus, an array of identical (or different) sensors may be produced in a relatively small substrate, enhancing the reproducibility and diversity of the sensor microsystem. Microfabrication technology includes photolithographic reduction, photoresist patterning, thin-film deposition, and wet chemical and dry reactive ion etchings. These techniques are mature and effective in the fabrication of the sensing elements of a microsystem. Photolithographic reduction can produce pattern with linewidth in the order of microns and in various forms of geometrical design. Thin-film deposition defines the layers of sensor structure or deposits the sensing materials and is accomplished by physical or chemical vapor deposition. The film may be metals, metal oxides, semiconductor materials, and insulation layers used extensively in chemical and gas sensor development. The thickness of a film can be closely controlled and may vary from a few angstroms to microns. Wet and dry etching in conjunction with photoresist patterning lead to the definition of highly reproducible, geometrically well-defined microsensor structures.

While microfabrication technology focuses on two-dimensional planar structures, generally, micromachining is defined as the means to produce three-dimensional structures that may be processed by bulk or surface micromachining. Examples include chemical anisotropic and dry etching, the sacrificial layer method, and LIGA (lithographic, galvanoforming, abforming) techniques. Chemical anisotropic etching depends directly on the crystalline lattice structure. For silicon etching, potassium hydroxide (KOH) and tetramethylammonium hydroxide (TMAH) solutions are the most common etching reagents. Dry etching processes include ion milling, plasma etching, or reactive ion etching and are not limited by the crystalline structure of the substrate. The sacrificial layer method employs a deposited underlayer that can be chemically removed resulting in cantilever or chamber box-type structures. LIGA techniques produce high aspect ratio microstructures. These micromachining techniques produce three-dimensional structures.

The combination of microfabrication techniques with micromachining may be used to fabricate a range of chemical sensor structures or platforms. Microfabrication of chemical sensors is not merely making a macrosize sensor smaller. The processing to produce a sensor material as a bulk material can change considerably when production of the material as part of a miniaturized system is demanded. However, successful MEMS technologies may batch process many sensors with reproducible features and improved capabilities.

Platform Technologies for Chemical and Gas Sensors

Detection of chemical and gas compositions may be accomplished with different sensing principles. No single sensing technology can effectively detect all chemical and gas components. Rather, selecting sensing approaches from a group of platform technologies best addresses a sensing need. A platform, as meant here, is a basic sensing structure formed by microfabrication technology. This structure can be tailored to optimize detection of a given problem. For example, the microfabricated pattern for an electrochemical cell can be formed and repeatedly fabricated. However, varying the selection of electrolyte and electrodes to be deposited in the microstructure may result in very different gas sensors. The development of four sensor platforms produced by microfabrication and micromachining technology, Schottky diodes, metal oxide semiconductors, electrochemical cells, and calorimetric devices, is discussed here. These platforms detect a range of species that are relevant in many practical applications.

Schottky Diode-Based Sensors

A Schottky diode is composed of a metal in contact with a semiconductor

or a metal in contact with a very thin barrier layer on a semiconductor.[5] The semiconducting properties of the silicon enable sensor operation. The diode characteristics are such that current can flow easily in one direction and be restricted in another direction. The metal layer serves as a gate for the diode. When a gas component absorbs selectively on the surface of the gate layer, the Schottky energy barrier changes and this change is measured and correlated with the gas concentration. The diode operates in a mode in which the response to changes in gas concentration is exponential.

A Schottky diode-based hydrogen gas sensor has been developed,[1,6] which employs a palladium-alloy gate and the sensor is fabricated with silicon-based processing techniques. Figure 1a shows the sensor structure. Hydrogen may be absorbed selectively in a palladium-alloy gate, thus lowering the Schottky energy barrier.[5,6] The change in diode characteristics quantifies the hydrogen gas present. A platinum thin-film resistance temperature detector (RTD) and heater are integrated into the sensor structure. These permit the sensor to be operated at controlled elevated temperature, thereby enhancing the sensor response time.

The Schottky diode platform may be modified to detect a range of gases by altering the gate material or changing the semiconductor to, *e.g.*, silicon carbide. For example, changing the gate alloy changes the viable concentration range of detected hydrogen.[6] Hydrocarbons, which dissociate at higher temperatures, may be detected by replacing the silicon substrate with a high-temperature semiconductor such as silicon carbide.[7]

Resistors Based on Metal Oxide Semiconductors

Over the years, metal oxide semiconductor sensors have been developed for chemical and gas detection with tin oxide (SnO_2) the most widely used. The pioneering work on tin oxide-based chemical sensors done by Taguchi[8] and Seiyama and Yamozoe[9] demonstrated their effectiveness in gas sensing. Nanocrystalline tin oxide particles produced by sol-gel technology have improved chemical sensing properties over macrograined or bulk materials. The capability to spin-coat and pattern sol-gel material consistent with microfabrication techniques enables integration of these nanomaterials into microchemical sensors.[10-14] The response of the metal oxide sensor is typically a fractional power law dependence to a gas such as hydrogen.

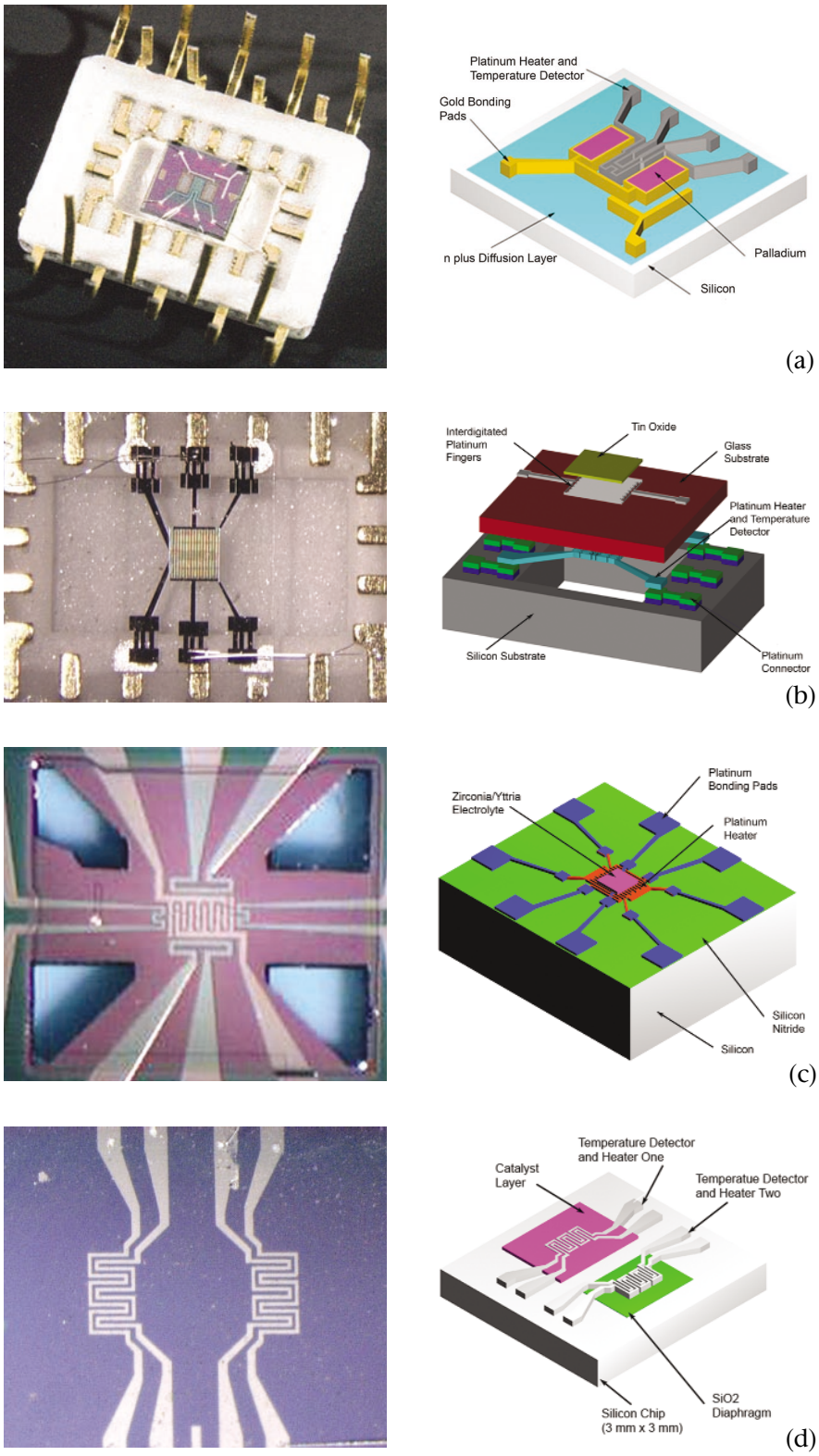

Fig. 1. Chemical sensing platforms: (a) Schottky diode-based microsensor (hydrogen sensor); (b) an interdigitated finger resistor sensor (thin-film tin oxide sensor); (c) solid electrolyte sensor (oxygen sensor); and (d) calorimetric sensor (hydrogen and hydrocarbons). Basic sensor platforms can be tailored for different sensing applications by choice of factors such as sensing material, substrate materials, and operating temperature.

Figure 1b shows a tin oxide-based gas sensor that relies on nanocrystalline tin oxide particles and is made by microfabrication and micromachining techniques. In contrast to the Schottky diode, the substrate is not part of the active sensor and the complete sensor may be produced from different sub-

component materials depending on the operating temperature of the application. A platinum thin-film resistant heating element was integrated into the sensor permitting the sensor to be operated at elevated temperatures. Micromachining techniques remove a sufficient quantity of the silicon substrate to selectively minimize thermal mass loss. Consequently, sensor operation at 350-400°C at a heating energy of 80-120 mW is achievable which is orders of magnitude smaller than the heating energies of conventional metal oxide-based sensors. Tin oxide-based sensors have been used for the detection of H_2, CO, H_2S, and CH_x. Selectivity and sensitivity of the sensor can be enhanced if proper catalysts can be incorporated in the nanocrystalline tin oxide thin films.

Electrochemical Sensors

Sensors operated on electrochemical principles have been developed for chemical and gas detection. The operating principles of electrochemical sensors include

- Conductivity measurement
- Potentiometric measurement
- Voltammetric and amperometric measurements
- Ion-selective detection

Figure 1c shows the design of a microfabricated yttria-stabilized zirconia (YSZ) solid-electrolyte oxygen sensor.[11] The platinum cathode and anode as well as the YSZ electrolyte were formed by ion beam sputtering techniques. A platinum thin-film resistance-type heating element permitted the sensor to be operated at temperatures as high as 600°C. The reduction of oxygen at the cathode results in a reducing current that is used to quantify the oxygen present.

By choosing the material that comprises the cell, different gases may be detected. For example, while YSZ can be used for O_2 detection, cation and proton conductors, such as alkali metal sulfates of lithium, sodium, and potassium, and NASICON (a sodium superionic conductor), show good cation conductivity at high temperatures. These materials can be used in the development of solid-state electrolyte electrochemical sensors, *e.g.*, a NASICON-based electrochemical sensor in a three-electrode configuration was used for CO_2 detection.[12] The gases detected in part depend on the operating voltage of the cell and this can be used to improve the selectivity of cell to certain gases. Electrochemical cells typically have logarithmic responses to changes in gas concentrations.

Calorimetric Sensors

Calorimetric sensors detect the amount of heat released by a combustible gas oxidizing in the presence of oxygen. This heat may help quantify the combustible gas present. Pellistor is a form of the calorimetric sensors that employs two temperature detectors, one detector coated with catalyst for the combustible gas. When the temperature detectors are heated, normally to around 400°C, the combustible gas is then oxidized on the catalyst-coated detector resulting in a temperature increase on this detector. The difference in the temperature measured by these two detectors is then used to quantify the combustible gas present. However, standard fabrication of pellistor-type sensors may be labor intensive and costly.

MEMS technology has overcome the shortcomings of manufacturing techniques to make a calorimetric sensor and enhance its performance at the same time. The design of such a calorimetric sensor is shown in Fig. 1d. Thin-film resistance devices act as both heater and

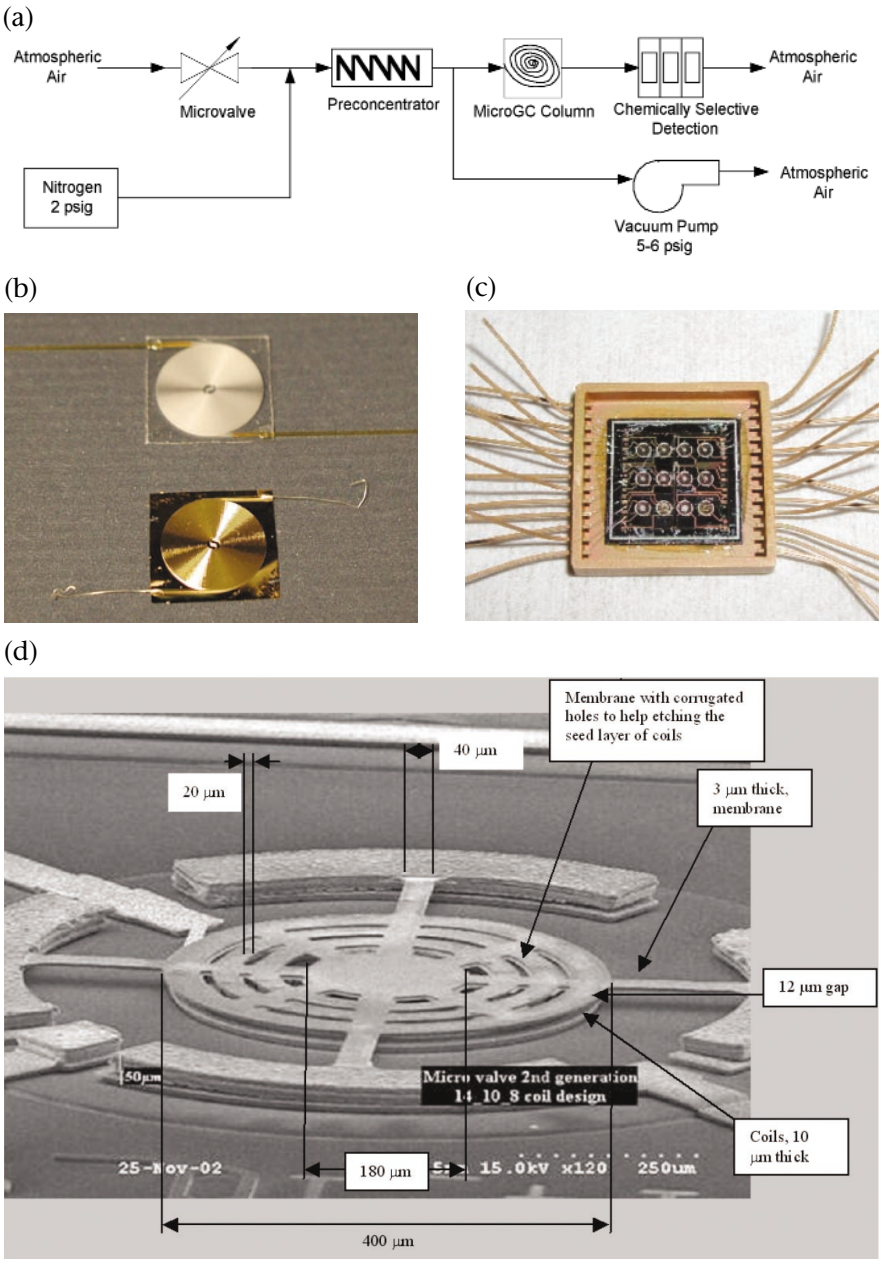

FIG. 2. (a) Schematic diagram of miniature GC system with microGC column with a preconcentrator and a chemical sensors array; (b) photograph of a microGC column with integrated heating element; (c) SEM micrograph of the 1 mm diameter microvalve with a 65 mm diam flow channel and 300 μm diam Permalloy disk, 8 turn gold coil; and (d) photograph of a 12 valve array in a flat package.

temperature detector. Etching techniques selectively remove part of the silicon substrate. This yields a thin silicon diaphragm or suspended trampoline structure minimizing thermal mass heat loss. Selective catalysts are deposited by physical or chemical vapor techniques. In this configuration, the heating and temperature detection functions are provided by different elements enhancing the control of heating and the sensitivity of the detection. The sensor is relatively small and requires low heating energy. The fabrication of these sensors can be cost-effective using batch processing techniques. However, catalytic combustion sensors are typically not selective with a response proportional to the amount of combustible gas given a sufficient oxygen concentration.

Microfluidics for Chemical Sensors (Microtechnology to Complement Microchemical Sensors)

The effectiveness of any particular sensor platform in an application is dependent on supporting technologies. For example, a lack of proper packaging, power, and device communication to the outside world can decrease the effectiveness of the sensor system no matter how effective the sensor. A microsensor that is then coupled with large, bulky, or inappropriate supporting technology can lose it effectiveness and ease of application. Microfabrication technology may produce supporting technologies as well as create a chemical sensing microsystem. One example is microfabrication technology for preconditioning the gases detected by a chemical sensor by passing them through a miniature gas chromatograph.

Since the pioneering work of Terry *et al.*[13] and the work of Reston and Kolesar[14] on miniature gas chromatograph (GC) systems there has been recent renewed interest in their development.[15-16] While conventional GC systems contain a fused silica capillary column, miniature GC systems utilize micromachined silicon channels that can be anodically bonded to glass plate. A μChemLab is under development at Sandia National Laboratories for the detection of chemical warfare agents and explosives.[14] An open-channel column provides advantages of rapid analysis but at the expense of resolution. Figure 2a shows a block diagram of the system, with a preconcentrator and a single separation column. The preconcentrator hot plate is coated with an adsorbent film to collect the sample, so that it can be released with a short thermal pulse into the column. Travel time within the GC of the analyte allows improved species differentiation.

One approach has utilized low thermal mass columns with an integrated heating element fabricated by vapor deposition into a micromachined silicon mold with parylene to achieve a system easily heated to the operating temperature using approximately 25-30 mW. Earlier work employed a silicon separation column formed by micromachining. The valve was either integrated or off-chip and the sensors were off-chip. One objective is to integrate all the GC components on a single wafer. The advantages of integration include the minimization of dead volume in the system, such that there is less peak broadening due to diffusion of the sample plug.

An important component in a miniature GC system is the valve to control flow. One approach to the microvalve system is based on the use of an actuator with latching ability to reduce power consumption. A miniature magnetic actuator is fabricated on a single silicon wafer with low-temperature complementary metal-oxide-semiconductor (CMOS) compatible processing. The coil and high permeability Permalloy films are deposited by electroplating into a photoresist mold. Additionally, motivation for this particular microvalve design is for the control of methanol/water based fuel mixture in a microfuel cell.[17] The com-

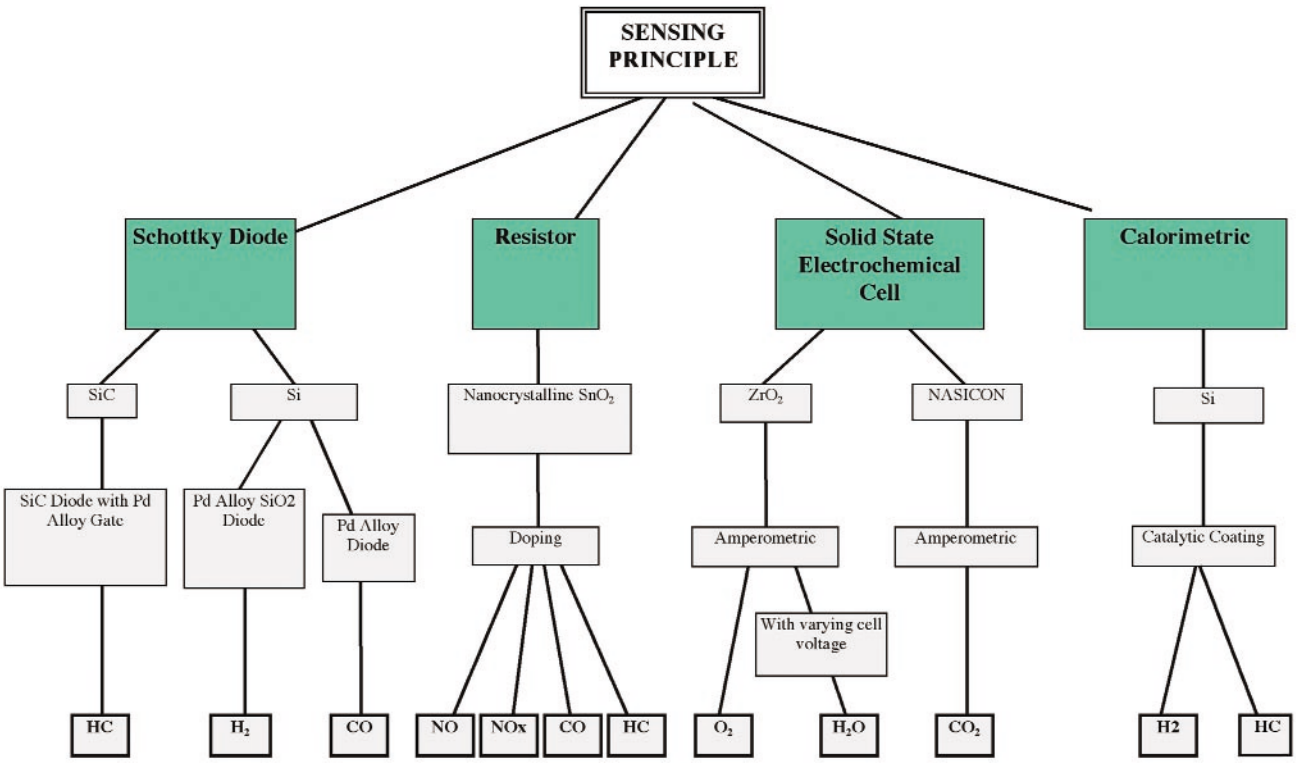

FIG. 3. Gas sensor platform technology. Given a limited number of platforms, a wide range of gases can be detected. Each platform is shown and the target detection species is noted for that configuration of the platform. (Reprinted with permission from Makel Engineering, Inc.)

plete structure of the valve is built on a single wafer and consists of three main parts: valve seat, gold coils, and membrane.[18] A permanent magnet in the membrane structure provides a bistable operation, where the permanent magnetic force holds the valve in its latching or closed position.[19] The microvalves are fabricated on top of a single wafer that uses eight mask steps. A scanning electron micrograph of the completed released valve structure is shown in Fig. 2b. The valves arrays can switch fluidic directions and the valve assembly can withstand leaks up to a pressure of 27 kPa. These micro GC systems coupled with microsensors provide new chemical sensing capabilities, which before were only available in large-scale systems.

Approaches to Real-World Problems

Various chemical sensor elements can be developed based on the MEMS-based platform technologies described above. Figure 3 (previous page) shows, in effect, a family tree of sensor platform approaches and the wide range of measurement options that may result from these platforms. Each platform has it own strengths, ideal range of application, and provides different types of information about the environment. For example, as noted above, different sensor platforms have different responses to the reactant gas (*e.g.*, exponential, logarithmic, and power law). Whatever platform or combination of platforms one uses, and how those platforms are tailored, depends on the needs of the application. Example considerations include

1. Does the application require high sensitivity or a broader range of detection (*e.g.*, Schottky diode *vs*. an electrochemical cell)?
2. Can application needs be met by careful choice of the operating parameters of the sensor (*e.g.*, choosing a proper voltage of an electrochemical cell) or is a combination of technologies needed to sort out the contributions of various similar species (*e.g.*, multiple metal oxide sensors operated in a nose configuration)?
3. Does the application operating environment require special materials or fabrication procedures (*e.g.*, a room-temperature application may use Si as a substrate while engine applications may require alumina or SiC)?

One practical example is hydrogen detection for leak detection applications. An approach to this application, which requires hydrogen detection over the range from parts per million to 100%, has been a hydrogen sensitive Schottky diode for low concentrations and a resistor for high concentrations.[1] In contrast, for emission applications in a mixed environment, a high-temperature array of sensors can be used: a SiC-based Schottky diode for hydrocarbon detection, a zirconia-based electrochemical cell for oxygen detection, and a doped tin oxide sensor for NOx detection.[1]

A wide range of other combinations, both of sensor platforms as well as supporting technology, are possible. Overall, the development of microsensor platforms provides a range of tools for users

to choose from in addressing a chemical sensing problem. Their minimal size, weight, power consumption, and integration into microsystems allow the use of the technology in applications where conventional technology may be inappropriate. One long-term objective is to provide smart sensor systems that may be tailored for the application, placed where they are needed, and provide full-field information on the process or event being monitored. ■

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