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Applications of Microfabrication Techniques in Electrochemical Sensor Development

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ABSTRACT

Electrochemical sensors have been used either as a whole or as an integral part of a chemical and biological sensing device. Microfabrication technology has been used in the development of electrochemical sensors. The recent advancement of micromachining techniques adds new impetus to electrochemical sensor development. Most noticable is the application of anisotropic chemical etching, plasma etching, sacrificial layer methods, and high aspect ratio X-ray lithography to enhance the opportunity to produce scientifically and commercially viable electrochemical sensors. Examples will be used to illustrate the potential of microfabrication and micromachining techniques in electrochemical sensor development.

Index Entries: Microfabrication techniques; electrochemical sensor development.

INTRODUCTION

Electrochemical sensors have been widely used in chemical and biological sensing. Generally, electrochemical sensors are categorized as conductivity, potentiometric, amperometric, and voltammetric sensors. Both amperometric and voltammetric sensors are characterized by the current-potential characteristics of the system and are less well defined. It

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is reasonable to consider amperometric sensors as a subclass of voltammetric sensors in which the current-analyte concentration relationship is obtained at a fixed electrode potential or electrochemical cell voltage.

All electrochemical sensors are basically an electrochemical cell using either a two-electrode or three-electrode configuration. Electrochemical sensors can be operated at various modes, such as steady-state or transient measurements. The general principles of electrochemical sensors have been extensively described in many electroanalytical references, and the selection of sensing techniques can also be found elsewhere. This article shall focus on microsensor development.

The introduction of microelectrodes to sensor design and the microfabrication of sensor electrode assemblies can be considered the most important developments in sensor technology in the past decades. The basic principles of microelectrodes have been known for more than half a century (since the introduction of the dropping mercury electrode in the 1920s), and the basic techniques of microfabrication of electronic devices became sophisticated during the past decades. Nevertheless, the merits of microelectrodes were not fully appreciated by electrochemists until the early 1980s and microfabricated integrated voltammetric sensors started to appear at approximately the same time. Thus, we are only at the threshold of the miniaturization and integration of sensor design.

The merits and virtues of microelectrodes or microelectrode arrays can be found elsewhere (*1,2*). This discussion shall focus on the microfabrication techniques applying to electrochemical sensor development.

MICROFABRICATION OF ELECTROCHEMICAL SENSOR ASSEMBLIES

Decided advantages that can be obtained through microelectronic fabrication of electrochemical sensors include reduced sensor size, reduced sample volume, reduced cost, and fast response time. Also, geometrically identical, highly uniform, and well defined electrode surface structures can be produced with microfabrication technologies. This is particularly attractive for voltammetric sensors. Photolithographic pattern reduction and thick-film (silk-screen printing) metallization techniques can be used in fabricating electrode patterns with a line width >50–100 μm. Ion-beam lithography can achieve a line width below 0.1 μm and X-ray lithography width below 20 nm. Therefore, basic microelectronic techniques can be considered sufficiently mature for microfabrication of sensor electrode assemblies.

Most of the electrochemical sensing elements involve noble metals, such as gold, platinum, and silver, and the deposition of these metals can be accomplished using thermal evaporation, plasma sputtering, ion-bean

coating, and chemical vapor deposition. These deposition techniques are also well established in microelectronic processing.

Although the feasibility and advantages of microfabrication of electrochemical sensors have been well demonstrated, few practical microfabricated electrochemical microsensors are evident. Progress in the development of microfabricated voltammetric sensors has been relatively slow. The first few publications describing the microfabrication of miniature oxygen sensors appeared around 1980 (*3–5*). Additional papers appeared after 1985 (*6–13*), using thick-film and/or thin-film technology for the fabrication of two- or three-electrode voltammetric sensors.

The microfabrication technology described previously is used quite effectively in the development of electrochemical sensors, including those mentioned above. Nevertheless, the sensors produced have basically a two-dimensional planar structure. Their limitations must be recognized.

Recent advancements in micromachining technology add new dimensions and impetus to electrochemical sensor development. Micromachining technology has been applied to the development of physical sensors, but its application to chemical or electrochemical sensor research has been very limited. It is believed that this technology will affect the advancement of electrochemical sensors significantly in the near future. Micromachining technologies include anisotropic chemical etching, plasma etching, the sacrificial layer method, and high aspect ratio X-ray lithography (LIGA). These techniques permit the formation of three-dimensional structures and other desirable features of electrochemical sensors, and will have a significant and revolutionary impact in future electrochemical sensor development. The microfabrication and micromachining technologies available now provide an excellent opportunity for electrochemical sensor researchers to advance this important scientific endeavor further and to make practical electrochemical sensors a true reality.

EXAMPLES OF MICROFABRICATED ELECTROCHEMICAL SENSORS

Microfabrication and micromachining technologies have been applied to the development of electrochemical sensors. A few examples will be used to illustrate the general approaches and advantages of these fabrication techniques. These examples are derived mainly from research in our own laboratories.

On-Chip Heater and Temperature Measurement Devices

The measurement of electrochemical sensors is temperature dependent. This temperature-dependent effect is predictable and is usually

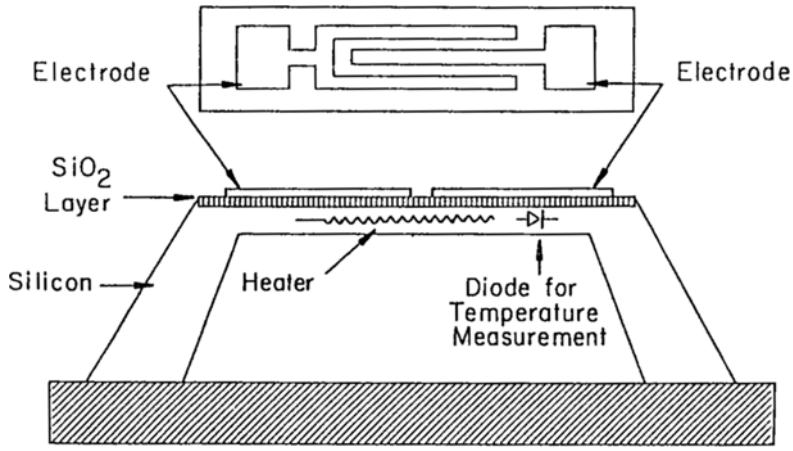

Fig. 1. Schematic structure of a micromachined electrochemical sensor.

compensated electronically. In this manner, a temperature measuring device, such as a thermistor, is placed in close vicinity to the electrochemical sensor. Because the characteristic of an electrochemical sensor is temperature dependent, operating the sensor at elevated temperatures may enhance the sensor response time. Moreover, when electrocatalysts are incorporated into the sensing element surface, operating the sensor at a selected temperature may enhance the selectivity and sensitivity of the sensor. Thus, it would be highly desirable to have the ability to control and measure the operating temperature of an electrochemical sensor. Consequently, an on-chip heating element and temperature detector integrated into the electrochemical sensor is logical. When silicon-based microfabrication technology is employed in producing electrochemical sensors, a silicon wafer 250 μm thick is typically used as the substrate. The thickness of the wafers may appear to be relatively small, yet they create a heat-mass loss problem that makes the control and measurement of the sensor temperature impossible. Figure 1 shows a schematic structure of a microfabricated electrochemical sensor that incorporates both an on-chip heating element and a temperature detector. In this sensor design, the backside of the silicon wafer is removed by anisotropic chemical etching. This reduces the total thickness of the silicon wafer from 250 to about 6 μm, on which the electrochemical sensor is formed. This results in a minimum of mass-heat loss, and the control of the operating temperature of the sensor can now be realized. The on-chip temperature heater can be a p-type or n-type doped silicon-resistant heater or a platinum-resistant heater, depending on the heating temperature required. Similarly, the temperature detector can be a p-n junction diode or a platinum-resistant thermometer, also depending on the detecting temperature range. The processes of doping the p or n-type silicon, the p-n junction diode, and the platinum-resistant heater and thermometer are all

known microfabrication techniques. By incorporating the concept of minimizing the heat-mass loss by anisotropic etching of the backside of the silicon wafer, a highly desired and practical electrochemical sensor can be fabricated.

This basic electrochemical sensor structure can be used for various applications. Electrocatalysts, such as platinum black or palladium, can be incorporated to provide selectivity. In essence, tin-oxide-based sensors can also be fabricated using this basic structure.

Solid Electrolyte Microoxygen Sensor

Calcia- and yttria-stabilized zirconia has been used as a solid electrolyte for a high-temperature electrochemical gas sensor for the monitoring of O_2, CO, H_2, SO_2, and others. Cation and proton conductors, such as alkali metal sulfates of lithium, sodium, potassium, and β-alumina, show good cation conductivity at high temperatures. Antimonic acid, zirconic phosphate, and dodecamolydo-phosphoric acid also exhibit good protonic conducitivity at ambient temperature, and have been used to detect low concentrations of hydrogen and carbon dioxide in air. Some of these solid electrolytes are used as substrates for microsensor fabrication.

High-temperature oxygen electrochemical sensors have been constructed using calcia- and yttria-stabilized zirconia, and operated in either the potentiometric or amperometric mode. The amperometric- or voltammetric-type oxygen sensor provides better sensitivity and detectable range than the potentiometric one. However, the amperometric or voltametric sensor must have a geometrically well-defined, highly reproducible electrode surface area. Microfabrication technology is a reasonable means to accomplish this. In our laboratory, an oxygen microelectrochemical sensor based on the amperometric mode of operation has been fabricated using microfabrication and micromachining techniques. Figure 2 shows the schematic structure of this device. Both the working and counter (reference) electrodes are platinum, and the heating and temperature-sensing resistant elements are also platinum. The yttria-stabilized zirconia film is deposited by the ion-beam-coating technique using a 9 mol % yttria-zirconia target. Because zirconium dioxide only becomes ionic conductive about 600°C, the sensor must be heated up to this temperature. The p- or n-type doped silcon-resistant heating elements are not usable above 250°C. Therefore, platinum-resistant heaters and temperature detectors are used instead. In order to minimize any mass-heat loss, anisotropic chemical etching is used to remove the backside of the silicon substrate on which the sensor is constructed. Preliminary tests show that this oxygen sensor can be heated up to 700°C and requires less than 2 W for the power consumption. This sensor prototype illustrates the feasibility of fabricating a practical high-temperature solid electrolyte electrochemical sensor using microfabrication and micromachining techniques.

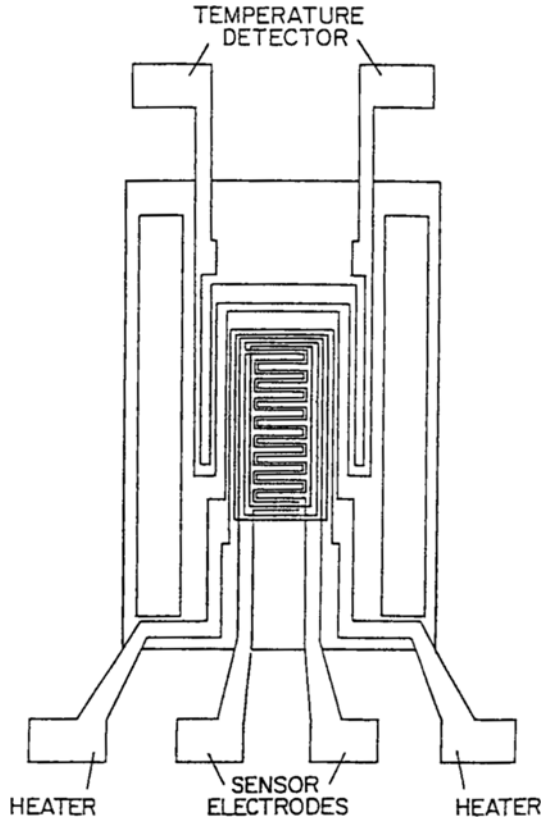

Fig. 2. Schematic structure of a micromachined solid electrolyte high temperature oxygen sensor.

POTENTIAL PROBLEMS ASSOCIATED WITH THE MINIATURIZATION OF ELECTROCHEMICAL SENSORS

The above discussion illustrates the potentials and the practicality of fabricating microsize electrochemical sensors using microfabrication and micromachining techniques. However, there are practical problems associated with the miniatruization of electrochemical sensors.

One of the obvious problems for voltammetric sensors is that the current output of a microelectrode decreases with its size. Magnitudes of signal from these microelectrodes are in the range of nanoamperes to picoamperes. In other words, the miniaturized sensor is equivalent to a signal source with high internal resistance and ac impedance. Complications as a result of that situation include:

1. The measurement of current may require more sophisticated instrumentation, since the bias current of most operational amplifiers is in the range of 10^{-8}–10^{10} A and that of the FET-input amplifiers of 10^{11}–10^{13}.
2. High noise generation and noise pickup: The thermo-noise of a resistance source—Johnson noise—is given by:

$$V_n = (4kT\,R\,\Delta f)^{1/2} \quad (1)$$

in which V_n is the noise level, k is the Boltzmann constant, T is the absolute temperature, R is the resistance, and Δf is the bandwidth of the measuring circuit. In addition, the magnitude of noise pickup from surroundings also increases with R.
3. The potentiostat circuitry may become unstable (oscillate) or completely fail to work when the source impedance and/or the noise level is too high.

Furthermore, the stability of microelectrodes is prone to be affected by chemical and electrochemical corrosion, since the mass of electrodes, especially those prepared by the thin-film technique, is usually very small. For example, the electroactive mass of a Ag/AgCl reference electrode can be exhausted by the seemingly small bias current (10^{12} A) of an FET-input amplifier after long-term continuous operation (*14*).

Further complications may arise when electrodes are packed too closely together. Chemical and electrical crosstalk between electrodes may not only distort the signal, but also seriously affect the stability of the electrodes.

1. The amplitude of a signal can be distorted when the product of a reversible electrode reaction can be reverted back to the original electroactive species at a nearby electrode and feedback to the sensing electrode (*15,16*).
2. The product or intermediate of an electrode reaction may diffuse to the surface of an adjacent electrode and attach it chemically. For example, the hydrogen peroxide (or HO_2-ion) formed as an intermediate of oxygen reduction reaction can be extremely harmful.
3. Capacitive electrical crosstalk between adjacent electrodes and connecting wires may short-circuit the signal (*17*) and give rise to instability of the control circuit (such as the potentiostat).

Therefore, a microelectrode assembly could be noisy and unstable if the size of individual electrodes is too small and electrodes are too closely packed. Thus, the ratio q/w between the distance, q, of two conducting paths to their width, w, should not be less than unity (*17*). Further theoretical and experimental studies are needed to clarify more precisely the possibility and limit of miniaturization of sensor electrode assemblies.

CONCLUSION

Microfabrication and micromachining technologies have demonstrated their applicability to electrochemical sensor development. The application of these techniques will add a new dimension and significant impact on sensor research. New scientific knowledge and practical devices will be realized through this fabrication approach.

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