CHEMICAL MULTISENSORS WITH SELECTIVE ENCAPSULATION OF ION-SELECTIVE MEMBRANES

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Abstract

Chemical sensors fabricated with simultaneous wafer-scale encapsulation of ion-selective electrode membranes are described. The sensors are miniature ion-selective electrodes in chambers located on a silicon substrate. These chambers are made by anodically bonding to the silicon a #7740 pyrex glass wafer in which cavities have been drilled. Pores with dimensions selectable from 50 μm upwards are opened in the roofs of the chambers by drilling with a CO_2 laser. Each sensor die contains four cavities which are filled under reduced pressure with liquid membrane material which is subsequently polymerized. The transducers on the cavity floor are Ag/AgCl electrodes. Interconnects between the sensor chambers on each die and bonding pads are made in the silicon substrate.

Introduction

In the past decade, many researchers have attempted to fabricate chemical and biochemical sensors with silicon integrated circuit technology. The appeal of using electronic technology in this way is the prospect of reducing sensor size and increasing the number of sensor functions as was achieved with purely electronic IC's. The device which has received most attention is the ion-sensitive field-effect transistor (ISFET) which first combined chemical sensitivity and electronic functions in one device. ISFET sensitivity to many analytes has been achieved by manually coating the gate with an appropriate ion-selective membrane.

The hand application of membranes introduces several problems, however. First, the advantage of wafer-scale processing of sensors is lost. Second, the size of each sensor is constrained by the accuracy of this manual operation, rather than by the limits of photolithography. Third, since the membrane sits on top of the sensor, it is mechanically vulnerable and adhesion to the ISFET insulator degrades in a few days. Indeed, the absence of a satisfactory technique for membrane encapsulation obstructs the commercial development of chemical sensors on silicon.

Several attempts to improve membrane encapsulation methods have been reported. Blackburn and Janata [1] reported a suspended polyimide mesh over the gate area to anchor the membrane. Sibbald *et al.* [2], Brown *et al.* [3] and Kimura *et al.* [4] have all used photolithographically defined wells in a thick layer of photoresist to hold manually applied membranes. These methods have improved sensor lifetime from a few days to a few weeks and may have reduced the mechanical vulnerability of the resulting devices. Hand application of membranes, however, is incompatible with miniaturization and mass production.

In this paper we present a new method for membrane encapsulation which attempts to overcome these micropackaging problems. Membranes are entirely enclosed within chambers. Pores in the ceilings of the chambers provide contact to the environment, while electrochemical transducers are located on the floors of the chambers. Chambers are filled with liquid membrane material simultaneously at the wafer level. Our first implementation of this general idea is illustrated in Figure 1. The special case with which we demonstrated the general technique may be modified in several details to further improve manufacturability.

Silicon Wafer Processing

To demonstrate this technique, we used the silicon substrate for two purposes: as a level for interconnecting sensors inside chambers to bonding pads outside chambers, and as a substrate for anodic bonding. Our sensor die consisted of four chambers, each containing, for simplicity, a Ag/AgCl electrode, within chip dimensions of 10×7 mm. Silicon wafers (p-type, 11–20 $\Omega\text{-cm}$) were processed as follows:

1. Initial oxidation (4700 Angstroms);
2. Photolithographic patterning of the oxide;
3. Implantation of arsenic ($6 \times 10^{15} \text{ cm}^{-2}$);
4. Removal of all the initial oxide, followed by growth of a new 0.5 μm SiO_2 layer;
5. Deposition and doping of polysilicon (0.5 μm , 20 Ω/square);
6. Photolithographic patterning of the polysilicon bonding ring;
7. Photolithographic patterning of contact openings to interconnects;
8. Deposition and photolithographic patterning of silver electrodes;
9. Photolithography and chloridation of silver electrodes in ferric chloride solution.

Figure 2 shows a die before silver chloridation.

Chamber Fabrication and Filling

We fabricated chambers by mechanically drilling an array of cavities in pyrex glass wafers and anodically bonding the glass wafers to the silicon wafers. Fabrication proceeded as follows:

1. Mechanical drilling of cylindrical cavities in optically polished, 650 μm thick #7740 pyrex wafers. Either of two diameters (1.8 mm and 2.7 mm) of diamond drills were used to drill an array of cavities 400 μm deep. Depending on drill diameter, cavity volumes were 1 or 2.5 μl . Figure 2 is an SEM picture of the interior of a cavity produced by a coarse drill; smoother surfaces are produced with finer drills.
2. Anodic bonding (at 400°C, 800 V) of pyrex and silicon wafers with cavities aligned over the electrodes.
3. Laser drilling of pores through the ceilings of the chambers. A 20W CO_2 laser ($\lambda = 10.6 \mu\text{m}$) with a focused spot size of 50 μm and a stepper-motor controlled XY-table with 5 μm spatial resolution were controlled automatically by a microcomputer [5]. Each pore was made with a burst of 100 μs laser pulses. Arrays of pores of various diameters can be achieved; an array of five is visible in Figure 3. Each pore is funnel shaped, as shown in Figure 4.
4. Filling the chambers with liquid membrane material. Liquid membrane material (positive photoresist in this case) was roughly spread over pores on the top of the glass wafer. The bonded wafers were placed in a bell jar and the jar pumped down to -600 torr gage pressure. After holding the bell jar at that pressure for 10 minutes, the jar was vented to atmosphere. Atmospheric pressure is sufficient to fill the depressurized chambers with aqueous or hydrophilic solutions.
5. Membrane polymerization.
6. Dicing and electrical bonding

Comments on the Technique

The principle of making ion-selective electrodes by covering Ag/AgCl electrodes with ion-selective membranes has recently been demonstrated by Rhodes [6]. The resulting structure is similar to a coated wire electrode. Our scheme allows the additional making amperometric measurements by means of a suitable metal electrode instead of the Ag/AgCl electrode.

Many variations on this general idea come quickly to mind. Clearly, either ISFETs or a variety of metal electrodes could be used as electrochemical transducers, and any aqueous or hydrophilic membrane material could be utilized. The technique is also compatible with on-chip signal processing circuitry. Sequential drilling of cavities in glass wafers followed by anodic bonding will probably prove to be less desirable than simultaneous anisotropic etching of cavities in silicon wafers followed by an alternative bonding technique. In that case, pores could be selectively drilled in silicon with a YAG laser. The impedances of individual electrodes may be trimmed during fabrication by varying the number of pores. Nothing about this technique restricts the number of chambers which may be accommodated in a given die. Furthermore, iteration of steps 3-5 of the chamber fabrication and filling procedure, with different chambers perforated in each iteration, permits several different selective membranes to be encapsulated on the same die.

More work is needed to explore the advantages, disadvantages, and optimal conditions for this approach to membrane encapsulation. For example, the best compromise between membrane enclosure for long lifetime and membrane exposure for low impedance remains to be determined. So, too, is the minimum practical chamber volume. Nor is the optimal drill coarseness for membrane adhesion known at present. The suggested variations on the chamber fabrication technique for improved manufacturability should also be tested. We are confident, however, that a variation of this general method will solve the micropackaging problems which have obstructed the practical implementation of integrated sensors utilizing chemically selective membranes.

References

- [1] G. Blackburn and J. Janata, *J. Electrochemical Soc.*, **129**, 2580 (1982).
- [2] A. Sibbald, P.D. Whalley, and A.K. Covington, *Anal. Chim. Acta*, **159**, 47 (1984)
- [3] R. Brown, R.J. Huber, D. Petelenz, and J. Janata, *Int. Conf. on Solid-State Sensors and Actuators*, Philadelphia 1985, p. 125.
- [4] J. Kimura, T. Kuriyama, and Y. Kawana, *Int. Conf. on Solid-State Sensors and Actuators*, Philadelphia 1985, p. 152.
- [5] L. Bowman, J.M. Schmitt, and J.D. Meindl, in: *Micromachining and Micropackaging of Transducers*, C.D. Fung et al. Editors, Amsterdam:Elsevier 1985, p. 79.
- [6] R.K. Rhodes, *IEEE Trans. Biomedical Eng.*, BME-33, 91 (1986)

Figure 1. Diagram of the structure of the membrane chambers and the Ag/AgCl electrode.

Figure 2. Silicon wafer with four electrodes and bonding pads before the glass wafer is bonded to it.

Figure 3. Interior view of a mechanically drilled, 2.7 mm diameter glass cavity with laser-drilled pores of different sizes in the upper surface.

Figure 4. Outside view of a pore drilled through the roof of a chamber.