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CONF-980918--
**Microfabricated silicon gas chromatographic micro-channels:
fabrication and performance**

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ABSTRACT

Using both wet and plasma etching, we have fabricated micro-channels in silicon substrates suitable for use as gas chromatography (GC) columns. Micro-channel dimensions range from 10 to 80 μm wide, 200 to 400 μm deep, and 10 cm to 100 cm long. Micro-channels 100 cm long take up as little as 1 cm^2 on the substrate when fabricated with a high aspect ratio silicon etch (HARSE) process. Channels are sealed by anodically bonding Pyrex lids to the Si substrates. We have studied micro-channel flow characteristics to establish model parameters for system optimization. We have also coated these micro-channels with stationary phases and demonstrated GC separations. We believe separation performance can be improved by increasing stationary phase coating uniformity through micro-channel surface treatment prior to stationary phase deposition. To this end, we have developed microfabrication techniques to etch through silicon wafers using the HARSE process. Etching completely through the Si substrate facilitates the treatment and characterization of the micro-channel sidewalls, which dominate the GC physico-chemical interaction. With this approach, we separately treat the Pyrex lid surfaces that form the top and bottom surfaces of the GC flow channel.

Keywords: gas chromatography, gas separations, micromachine, high-aspect ratio Si etch (HARSE), deep reactive ion etch (DRIE), open capillary, stationary phase, micro-column, micro-channel

1. INTRODUCTION

Due to the utilization of open capillary tubing, gas chromatographic (GC) separation is used extensively today in a number of environmental and industrial applications. Open capillary tubing, in contrast to previously used packed columns, increases resolving power, speed of separations, and column efficiency. A number of researchers have investigated microelectronic fabrication techniques to duplicate the advantages of capillary tubing GCs in a significantly smaller device. In this approach, micro-channels are etched into silicon or fused silica wafers and sealed with lids anodically or fusion bonded to the substrate. Microfabricated devices have a number of potential advantages compared to conventional GCs, including: small size; low manufacturing cost; minimum dead volume when integrated with microsensors; and, most significantly, flexibility in design and fabrication for optimized performance in a variety of applications.

Two issues are particularly important in the design and fabrication of GCs, both microfabricated and conventional. The first is column dimensions: total column length and capillary diameter or micro-channel width and depth. As the channel becomes narrower, more gas is exposed to column walls and the diffusion distances become shorter. This increases the interaction with the stationary phase, decreases the required column length and leads to a shorter analysis time. However, a significant pressure drop develops as the channel becomes quite narrow, requiring increased performance from the pumping system. In our particular application, we are limited by the performance of currently available miniature pumps to about 6 psi of vacuum to pull gases through the micro-channel. To determine the optimum channel size, we have fabricated micro-channels from 10 to 80 μm wide, 200 to 400 μm deep, and 10 to 100 cm long using both wet and plasma etching processes. Micro-channels up to 100 cm long fit in a surface area of 1 cm^2 . Gas flow and GC performance were measured to optimize our design and to establish a model for predicting future designs¹.

The second issue is the uniform deposition of a stationary phase coating that provides the physico-chemical interaction to separate the gas species. Deposition uniformity has been a difficult process for both capillary tubing and micro-channels. Microfabrication, however, may be advantageous since surfaces can be easily processed prior to required coatings in comparison with commercial microcapillary tubing. Our approach to uniform stationary phase deposition for high aspect

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ratio channels is to etch through the silicon wafer, thereby accessing, from both sides of the wafer, the etched surfaces that subsequently form the primary channel wall surfaces. With this method, different surface treatments for channel top and bottom surfaces can also be utilized.

2. GAS CHROMATOGRAPHY COLUMN FABRICATION

We have employed both wet and plasma etching techniques to form deep micro-channels in Si wafers. Anisotropic wet etching produces smooth, well-formed channel sidewalls but is restricted to specific crystallographic orientations. Lithographic masking is also somewhat more involved than for plasma etching. In contrast, plasma etching is independent of orientation and lithographically less complex but sidewall roughness and etch residues are more significant. After etching, channels were sealed with Pyrex lids anodically bonded to the Si substrates and micro-capillaries were attached to the GC inlet and outlet for testing.

2.1 Wet etched GC micro-channels

For the wet etched GC devices, we used (110) Si wafers that etch anisotropically to form vertical channels with (111) sidewalls². Two sets of (111) planes exist normal to the (110) wafer surface making angles of 70.5° and 109.5° to the wafer flat. When the direction of the micro-channels lies along a (111) plane, large depth to width aspect ratios of 200:1 can be formed². For channel alignment, we designed an alignment structure that was patterned in the wafers prior to channel fabrication. This asterisk-shaped structure had lines oriented in 1° increments to the (111) planes. Once etched, the correct orientations for the channels can be determined by finding the alignment mark with the narrowest linewidth. For example, after etching 50 μm, the linewidth difference was about 3 μm per degree of rotation.

For the micro-channels, we designed serpentine channels 10, 20, and 40 μm wide and 12 to 80 cm long with channel segments parallel to one of the (111) planes. Since outside corners do not etch like straight runs because of solution exposure to two surfaces, we minimized the number of corners in the GC serpentine devices to two per centimeter of channel length. To fabricate channels, wafers were first coated with PECVD SiO₂, the alignment structures were patterned with standard photolithographic processes, and then the oxide was plasma etched. The resist was then removed and the silicon was etched in a 50% KOH solution at 80°C to maximize etch anisotropy.³ After the alignment mark etch, the process was repeated using the channel mask. Channels were etched to a depth of 80 μm and the SiO₂ mask was removed.

2.2 Plasma etched GC micro-channels

For our plasma etched GC column fabrication process, we configured deep narrow channels in circular spiral patterns. The mask design contained spiral channels with widths of 10, 40, and 80 μm, lengths of 10, 30, and 100 cm and spacing between channels from 1 to 4 times the width. For the plasma etch process, only patterned photoresist is required for masking. The resist etch rate compared to Si is about 1:50, so a 10 μm thick resist is adequate for a 400 μm deep Si etch⁴. AZ4903 resist was used on 3 and 4 inch diameter (100) silicon wafers. Patterned wafers were etched from 200 to 400 μm using a high aspect ratio Si etch (HARSE) plasma process developed by Bosch⁵ that cycles between etching and an inhibitor polymer deposition to maintain nearly vertical channel sidewalls during the etch.⁶ During the etch steps, Si is preferentially eroded away from channel bottoms relative to the channel sidewalls due to the high plasma bias. Between etch cycles, an inhibiting polymer is deposited to further minimize lateral etching. After the etch, the photoresist is removed from the wafer using either acetone or sulfuric acid/hydrogen peroxide solution. Although the plasma etch process requires specialized plasma equipment, we find that its independence of crystallographic orientation and simplified lithographic masking makes this approach preferable to the wet etch process.

Lateral undercut of the etch mask is about 1.8% of the depth for a nominal 40 μm wide channel, as determined from SEM profiles (typical profile shown in Fig. 1). Channels are wider at the top due to erosion of the sloped thick resist profile. The depth was uniform over the length of each micro-channel, but etch depth varied depending on the spiral pitch, presumably due to etch loading effects. Surface roughness is apparent at the top and bottom of the etched sidewalls (Fig. 2). This is best described as narrow striations several microns long in the direction of the etch. From detailed analytical work, we find that the roughness near the bottom of the channels is correlated to the presence of a monolayer of the inhibitor

polymer. These surface abnormalities are of concern with respect to uniform deposition of stationary phase coatings in later processing steps.

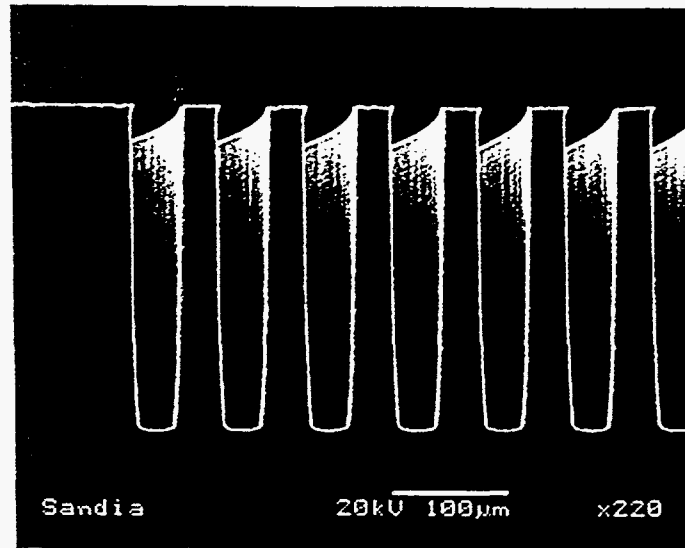


Figure 1 Cross section of a 40 μm wide spiral GC etched 270 μm deep using the high aspect ratio silicon etch (HARSE).

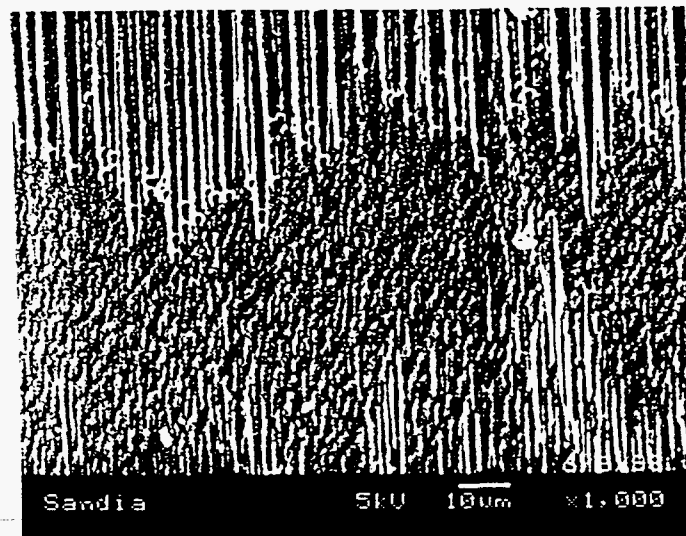


Figure 2 Roughness variation shown on a HARSE channel sidewall.

2.3 Lid Attachment

Following silicon channel etching using both wet and plasma processing, open channels were sealed by anodically bonding machined Pyrex lids to the Si substrate. Inlet and outlet access holes 375 μm in diameter were ground through 1 mm thick Pyrex wafers, followed by a sulfuric acid/hydrogen peroxide clean of both the Si and Pyrex wafers. The lids were aligned to the silicon channel by placing the access holes over the channel ends, the assembly was heated to 305°C, and 1800 volts were applied across the assembly. We bonded near 305°C because this provided the best match of thermal expansion in the two materials⁷. We found this bond, which is believed to be a combination of static forces due to ionic displacement and

chemical oxidation due to oxide evolution from the glass,⁷ to be a good hermetic seal, as well as robust for both individual die and whole wafer assemblies. In the case of whole wafer bonding, sawing to separate die was accomplished without degradation of the bond.

In order to introduce gases into the anodically sealed channels, we attached short lengths of 350 μm diameter capillary tubes to the 375 μm holes in the Pyrex lids. For flow measurements and subsequent modeling work, capillary connectors were attached to the glass using RTV silicone adhesive to form a fillet seal at the gap. With respect to stationary phase deposition, detailed tests were performed to determine which adhesive materials would be most compatible with chloroform solutions. From hardness testing and mass loss, we found epoxies, as opposed to silicones or silicates, were most resistive to dissolving or softening in the test solutions, and a clear UV epoxy is currently being employed for the GCs as well.

3. STATIONARY PHASE DEPOSITION AND GC SEPARATION

Inside surfaces of GC columns usually require deposition of films that produce the separation of interest. These films are typically referred to as stationary phases since a molecule is stationary when it is sorbed into this material in contrast to being mobile when it is in the gas flowing through the column. Commonly used stationary phases consist of polymers synthesized with specific chemical groups with the proper physico-chemical interactions to cause separation of the gas species of interest. A nonpolar stationary phase for example, usually separates compounds in relation to their boiling point, so pentane, with the lower boiling point, would elute before hexane. A polar stationary phase would preferentially retain polar compounds, allowing the nonpolar components to elute first, followed by the polar components.

We have used conventional stationary phase deposition techniques to coat the micro-channels. In one approach, a plug of the stationary phase material is pushed through the channel with pressurized gas. In a second approach, the channel is first filled with the stationary phase material and then the excess is removed by applying a vacuum to the end of the channel. Although the second method resulted in a thicker coating and better separation performance, neither method resulted in uniform film deposition or the expected level of performance. Increased separation power can be expected as improvements are made in the coating process. Techniques for improving stationary phase coating are discussed below.

In our application, we are interested in the separation of chemical warfare agent simulants from common interferants. We expect that a low polarity stationary phase such as polydimethylsiloxane (OV1) to be one phase that will provide useful separation. Figure 3 shows an example of a separation of dimethyl methyl phosphonate (a nerve agent simulant) from two common hydrocarbon compounds (typical of interferants). The chromatogram shows that these compounds can be effectively separated on the OV1-coated micro-channel GC in just under two minutes. Other experiments have shown that the separation can be completed in less than 30 seconds with optimized temperature control. Although good separation is noted in Fig. 3 by baseline resolution of the three compounds, calculated column efficiency (theoretical plates) is somewhat low compared to conventional capillary columns. We attribute this to non-uniform stationary phase coating.

The characteristics of the GC surfaces prior to stationary phase deposition play an important role in the uniformity of this coating and, therefore, the performance of the GC. We are using microfabrication techniques to modify the micro-channel surfaces in order to study the impact on the stationary phase. We have employed Si etches and Si oxidation to this end. In order to evaluate the effect of these processes on the micro-channel surfaces, we have developed spiral channels that are etched (using HARSE) completely through the Si wafer. This provides a uniform access for the surface-modification chemicals to the channel sidewalls.

We have taken two approaches for etching micro-channels completely through Si wafers. In the first approach, the GC wafer is attached to a Si carrier wafer with photoresist. After etching through the GC wafer, the carrier is removed by soaking the wafers in acetone to remove the resist and release the wafers. In the second approach, the Si wafer is anodically bonded to a Pyrex wafer carrier. After etching through the Si wafer, the Pyrex carrier is removed by soaking in HF. This second technique is preferred for long etches through thick Si wafers, where the high temperatures in the etch chamber can cause the resist adhesion layer to fail and expose the underside of the GC wafer to the etch plasma. This roughens the bottom surface of the wafer, making lid attachment difficult. As shown in Fig. 4, the through-etched micro-channels do not sag out of plane and are adequately robust for additional processing.

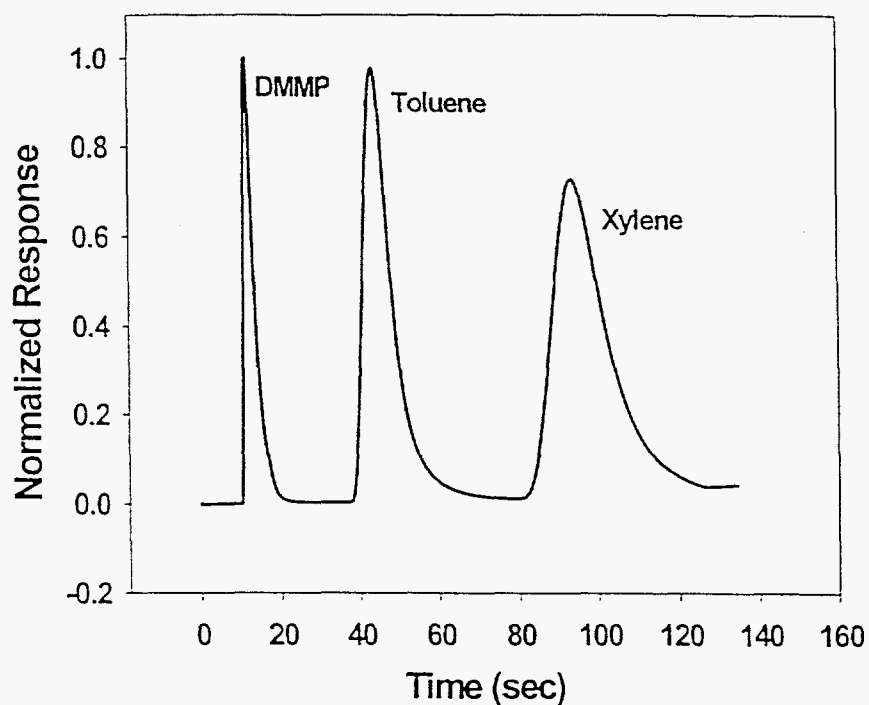


Figure 3 Separation of dimethyl methyl phosphonate from toluene and xylene using a 1 m long, 40 μm wide, 250 μm deep micro-channel GC. Operating conditions are 40 C isothermal and 4 psig N_2 carrier gas. The stationary phase is OV1 (polydimethylsiloxane).

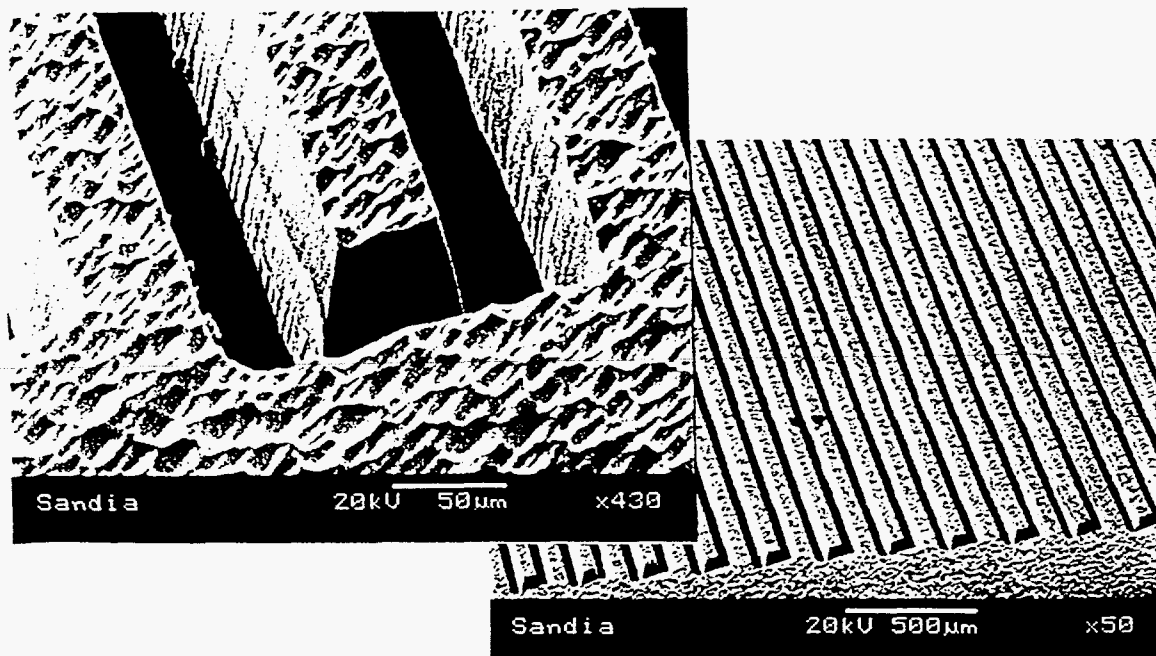


Figure 4 Micro-channels etched completely through a 125 μm thick silicon wafer using HARSE remain in the plane of the wafer.

To treat the through-etched channel sidewalls to reduce roughness and create a uniform surface before stationary phase deposition, wet etching and dry oxidation are being investigated. Both KOH anisotropic etching and a HF/HNO₃/CH₃COOH polishing etch (with high HNO₃) reduced HARSE roughness. However, these etches also increase roughness of top and bottom wafer surfaces, making lid anodic bonding difficult. Other masking layers applied prior to the HARSE process may be able to protect the top and bottom wafer surfaces from the subsequent wet etch.

Following the wet etch to reduce sidewall roughness, the sidewalls are thermally oxidized to produce a silica surface similar to that of fused silica capillary tubing. SiO₂ layers up to 1000 Å thick have been formed on the sidewalls with thickness uniformity to within 2%. No adverse stress effects were observed.

To seal the through-etched channels, we have demonstrated anodic bonding of Pyrex wafers on both the front and back surfaces of the oxidized Si wafer. Care must be taken to avoid contamination of the second Si surface during the bonding of the first surface. Parameters for both bonding steps were similar, and no differences in bonds on the top and bottom of the device were observed. An additional advantage to the through-etch approach is that we can place chemically distinct surfaces, as compared to Si and SiO₂, on the narrow top and bottom edges of the micro-channels by coating the Pyrex surfaces with a layer of Au. By tailoring the stationary phase chemistry so that it does not bind to the Au surfaces, the micro-channel GC should closely approximate an ideal parallel plate GC.

4. SUMMARY

Using microfabrication techniques to produce GCs has a number of important advantages, including small size (1 cm² by 400 μm thick for a 1 m long column) and the ability to tailor the GC surfaces for optimized performance. We have produced micro-channel GCs using wet and plasma Si etching and sealed the channels with anodically bonded Pyrex lids. We have shown separation of chemical warfare agent simulants using a micro-channel GC coated with a stationary phase commonly used for capillary tubing. GC performance is somewhat lower than expected, probably due to non-uniformity in the stationary phase coating. To improve separation performance, we have developed fabrication techniques to establish well characterized starting surfaces before stationary phase film deposition and also to selectively deposit these films only on principal GC surfaces. The development of a plasma etch process that can cut micro-channels completely through a Si wafer has been key to this effort. Characterization of the micro-channel surfaces and development of stationary phase deposition techniques are on-going.

Measuring the flow characteristics of the micro-channel GCs has enabled us to develop a model for gas flow and GC performance in these devices¹ that will be used for future GC design. Model results allow us to determine the optimum channel width for a given length, pressure drop, and sample dead time. For example, with a 100 msec dead time and a 1.5 m column length, the maximum efficiency of 14,000 theoretical plates is achieved for a column width of 52 μm. GC performance is independent of the spiral pitch. Using our fabrication process, this micro-channel GC can be produced in an area of approximately 1.5 cm².

5. ACKNOWLEDGMENTS

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000

6. REFERENCES

1. M. L. Hudson, R. Kottenstette, C. M. Matzke, G. C. Frye-Mason, K. A. Shollenberger, D. R. Adkins, and C. C. Wong, submitted to 1998 International Mechanical Engineering Congress and Exposition, Nov. 1998.
2. D. L. Kendall, Ann. Rev. Mater. Sci. 9, 373-403 (1979).

3. D. L. Kendall and G. R. de Guel, *Micromachining and Micropackaging of Transducers*, edited by C. D. Fung, P. W. Cheung, W. H. Ko and D. G. Fleming, Elsevier Science Publishers B. V. Amsterdam, 1985.
4. Thick photoresist process: Spin AZ 4903 at 3500 rpm, soft bake for 4 minutes on a 120°C hotplate, wait 3 hours for resist rehydration, and, after exposure, develop in AZ400 diluted 1:4 with water.
5. Licensed from Robert Bosch GmbH patent number 5501893, issued March 26, 1996.
6. R. J. Shul, C. G. Willison, C. T. Sullivan, S. H. Kravitz, L. Zhang and T. E. Zipperian, *Electrochem. Soc. Proc.* Vol. 98-2, (1998) 564.
7. T. Rogers and J. Kowal, *Sensors and Actuators A* 46-47 (1995) 113.