



Etching technology for chromatography microchannels

R. W. Tjerkstra,* M. de Boer, E. Berenschot, J. G. E. Gardeniers,
A. van den Berg and M. C. Elwenspoek

MESA Research Institute, Twente University, P.O. Box 217, 7500 AE Enschede, The Netherlands

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Abstract—Half-circular channels, to be used for gas chromatography, were etched isotropically using a mixture of HF, HNO₃ and H₂O. Two wafers with half-circular channels were bonded on top of each other to yield channels with a circular cross-section. During etching the so-called “loading effect” was encountered: the etch rate depends on the local structure density. To solve this, extra structures were placed around the channels to create an equal structure density over the wafer and so prevent irregularities in channel width. To eliminate the alignment problems that arise when bonding two wafers with isotropically etched channels together, a method which combines deep trench etching, passivation and isotropic etching was developed to construct channels under the surface of a wafer. © 1997 Published by Elsevier Science Ltd

Key words: Isotropic wet etching, silicon micromachining, tubular channels, fusion bonding, buried channels.

1. INTRODUCTION

1.1 Gas chromatography

Gas chromatography is a routinely used technique in many analytical laboratories, because of the high resolution, selectivity and sensitivity that can be achieved. In fact, from the 1950 s until the invention of High Performance Liquid Chromatography (HPLC) in the 1980 s, it was the main used separation technique [1].

A gas chromatograph, like many other chromatography systems, consists basically of the components shown in Fig. 1. In a continuously moving gas stream called the mobile phase, a mixture of components is injected. This mixture is heated to a temperature above the boiling points of its components, and then transported to the separation column. The column is a tube that contains the so-called stationary phase. This stationary phase is responsible for the separation of the components in the mixture. It can be a solid or a liquid, which covers either the column wall (open tubular column) or the surface of tiny particles with which the

column is filled (packed column). In the column, the gaseous mixture is separated because the different components have a different affinity for the stationary phase. When a component of the sample mixture has a great affinity for the stationary phase, it will most of the time be adsorbed to it. If a component is not adsorbed to the stationary phase, it will flow through the column due to the movement of the mobile phase. So components with a high affinity for the stationary phase will travel more slowly through the column than components with a low affinity for the stationary phase. Eventually, the components leave the column and are detected by the detector.

The output of the detector is converted to a chromatogram, where the response of the detector is shown as a function of the time. The components with the least affinity for the stationary phase will reach the detector first. Ideally, the peaks have zero width, but because of, among others, the volume of the injected sample and diffusion, this cannot be achieved in practice. The gas chromatographs most commonly used today are equipped with open tubular capillary columns. These are mostly made of fused silica, with diameters of around 100–1000 μm , and lengths of up to 50 m.

*Author to whom correspondence should be addressed.

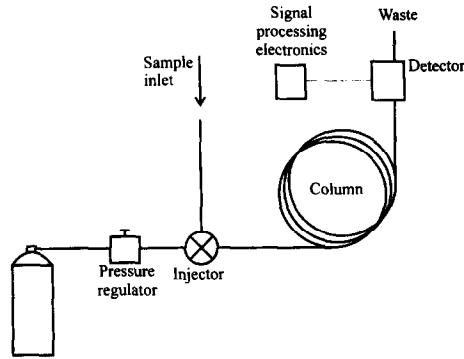


Fig. 1. Schematic drawing of the main components of a gas chromatograph.

1.2 Micromachined gas chromatographs

Micromachined gas chromatographs theoretically have many advantages compared to their bigger, normal counterparts. They use less energy and their size can in principle be reduced that of *eg* a large pocket calculator, so they can be used directly at the place where the sample is taken. This is of great importance for environmental analysis.

The first integrated micromachined gas chromatograph was constructed by Terry in 1979 [2]. It consisted of an injector, a 1.5 m long column, and a thermal conductivity resistor as a detector, all integrated on a 2" silicon wafer. No other micromachined gas chromatography system was reported until 1994 [3]. This system was specifically constructed to detect mixtures of ammonia and NO_2 . It consisted of a 0.9 m long column, an injector and two detectors (a thermal conductivity detector and a selective chemiresistor for the detection of NO_2 and NH_3).

The aforementioned gas chromatographs did not perform very well [4]. One of the reasons for this lies in the shape of their columns. Open tubular columns that were very wide compared to their heights were used. In such a column a particle that diffuses upwards or downwards from the middle of the column reaches the wall after a very short time, compared to a particle that starts at the same place, but moves in a horizontal direction. This causes the appearance of peak broadening. Also, in the corners of the channels dead volumes appear, causing a memory-effect that also manifests itself in peak broadening. In our opinion, columns with a circular cross section will perform much better because of the absence of corners and the equal diffusion times in lateral and vertical directions. In this article we show how circular micromachined columns can be made by two different methods: the etching of half-circular channels in two wafers that are then bonded on top of each other, and another method that uses deep trench etching and wet chemical isotropic etching to construct columns buried inside the wafer.

1.3 Silicon micromachining techniques

Silicon has material properties that make it very useful for the fabrication of micromachined structures [5]. Many of the techniques used for the construction of integrated circuits in microelectronics are applicable to silicon micromachining. Therefore silicon is the most commonly used material in micromachining.

In order to be able to etch structures in silicon, the material has to be covered with a "mask" material that etches much slower than silicon. Mostly silicon oxide or nitride is used for this purpose. After covering the silicon with the mask material, holes are etched into it, so the silicon can be etched locally. Silicon can be etched in various ways, for example by reactive ion etching (RIE) [6], electrochemical etching [7], and wet chemical etching. The various techniques used for the production of the silicon microchannels are discussed briefly.

1.3(a) RIE etching. In RIE etching a plasma is used to create reactive species (radicals and ions) that etch the silicon. Usually during etching the silicon surface is covered with a passivating layer of *eg* silicon oxide or silicon fluoride. This layer is partly removed by the incoming ions, creating "active sites" on impact. The radicals adsorb on these sites and react with the silicon, which is etched. The resulting products diffuse away from the surface and are removed.

With RIE etching, many channel shapes are possible, depending on the etching conditions: half-circular, rectangular, or with positive or negative tapering. Because of this versatility RIE is becoming more and more popular.

1.3(b) Chemical etching. Most of the chemical etching of silicon nowadays is one using solutions of KOH. However, silicon etches anisotropically in KOH solutions. The design of the structures is therefore restricted by the place and orientation of the slowest etching crystal planes. This chemical can therefore not be used to etch tubular channels. Schwartz and Robbins have investigated the etching of silicon with mixtures of HF, HNO_3 and H_2O [8]. Their article reveals that the etching reaction in



Fig. 2. Isotropically etched channels in silicon.

these solutions is primarily diffusion-controlled when the HNO_3 concentration is high, and the HF concentration is low. A solution that meets these criteria etches isotropically. We used a solution containing HF, water and HNO_3 in the relation 5 : 15 : 80 vol%. A 50% HF solution and a 69% HNO_3 solution were used. The mixture etches silicon isotropically, leaving half-circular channels with very smooth surfaces (Fig. 2). The surface roughness, as estimated from SEM pictures, is about 3 nm. The etch rate at 20°C is about 0.8–1 $\mu\text{m}/\text{min}$, depending on the structure density and mask opening size.

2. EXPERIMENTAL

2.1 Route I: isotropic etching and wafer bonding

The procedure for the construction of the channels is outlined in Fig. 3. Because two wafers are used to produce one column, the procedure is not the same for both wafers.

First, alignment marks are etched in the wafers using RIE etching. Because of limitations of the equipment used, one wafer has to have alignment marks on the back as well as on the front. The wafers we used for this were polished on both sides. After etching the alignment marks, the wafers are cleaned and a 500 nm thick LPCVD silicon nitride layer is grown on them. This nitride layer is then

patterned using RIE etching, after which the isotropic etching of the silicon can take place. Spiral-formed columns of around 10 m length were etched on 3" wafers. The mask opening was 10 μm wide. The final diameter of the channels depends on the etching time. The wafers were etched two at a time in separate beakers using the same, fresh etching solution for both wafers. After etching the channels the nitride is removed by immersing the wafers in a 50% HF solution for about two hours. The bonding process is described in Section 2.1(b).

2.1(a) The loading effect. After etching some wafers we discovered that the channels on the rim of the spiral had a larger diameter than the channels in the middle of the spiral. This is because on one side of the channel there is no silicon that etches and takes away fluoride ions. The ions above the mask material next to the outermost channels can diffuse to these channels (Fig. 4). This leads not only to differences in the channel diameters, but also the uniformity in the widths of the channels is worse on the rim of the spiral. This means channels of different widths may be bonded on top of each other, causing inhomogeneous coverage of the side wall and the appearance of dead volumes. Stirring the solution during etching proved to enhance the etching in the direction of fluid flows, yielding badly shaped channels. In an attempt to solve the loading effect problem, we surrounded the column

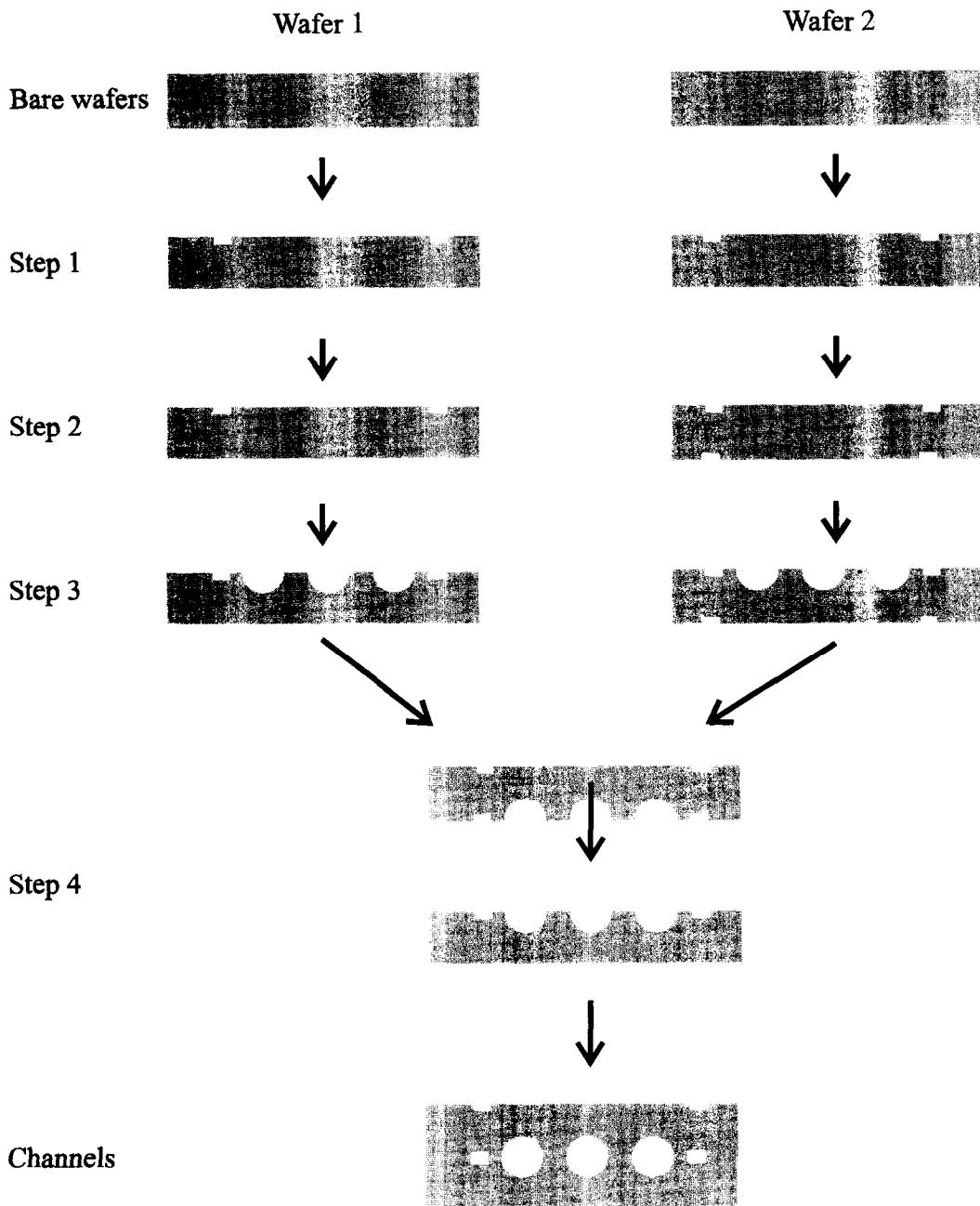


Fig. 3. Outline of the etching procedure for the chromatography columns.

with extra channels with the same width and the same distance from each other as the channels in the spiral. These extra channels take away the extra HF that otherwise causes the broadening of the outer channels. In order to determine the distance to which the extra structures have to stretch out, we used the article of Kuiken *et al.* [9], who investigated the theoretical aspects of mass transport during isotropic etching. The concentration of the dissolved chemicals as a function of the distance to the etching surface depends on the etch time. The bulk concentration is reached at a distance of

around $3(Dt)^{1/2}$, in which D is the diffusion coefficient, and t the time. With an etch rate of around $1\ \mu\text{m}/\text{min}$, it takes about an hour to reach the desired depth of the channels of $50\ \mu\text{m}$. With $D(F^-) = 1.5 \times 10^{-5}\ \text{cm}^2/\text{s}$ [10] and $t = 3600\ \text{s}$, we come to a distance $3(Dt)^{1/2}$ of $6900\ \mu\text{m}$. So the channel was surrounded with extra structures up to a distance of about 7 mm. The extra structures were also placed on the spaces inside the spiral.

2.1(b) Bonding of the wafers. For wafer bonding, various techniques are available [11]. Here we use silicon fusion bonding [12, 13]. For this method the

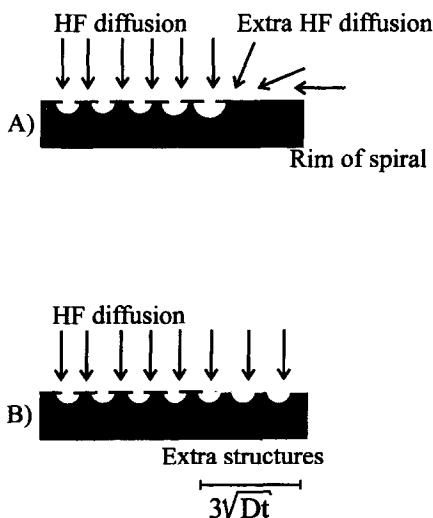


Fig. 4. Side view of the etched channels, showing the loading effect. In (A), the HF molecules that find themselves in the area next to the etching spiral can diffuse to the outer channels. These channels etch faster than the other channels due to the extra supply of HF. To reduce this effect, in (B) extra structures are placed around the spiral, that take away the extra supply of HF molecules. This results in an equal channel width in the spiral.

wafers are made very clean, using the following method:

1. Immersion into a solution of 75 vol% concentrated H_2SO_4 and 25 vol% H_2O_2 for 35 minutes.
2. Immersion into a solution of 1 vol% of a 50% HF solution in H_2O for 5 minutes.
3. Immersion into fuming nitric acid for 15 minutes.
4. Immersion into a 70% HNO_3 solution, temperature 95°C for 30 minutes.

After every step the wafers were thoroughly rinsed with de-ionised water. After cleaning, the bonding has to be performed immediately. The wafers were aligned with respect to each other using a mask

aligner, pressed together, and then annealed at 1100°C for two hours.

2.2 Route II: by RIE deep trench etching and isotropic wet etching

2.2(a) *Problems with the former procedure.* The proposed method for making chromatography channels is very simple and promising. It can be done in any clean room with moderate equipment. It contains some difficulties, however, rising from the fact that two wafers with half-circular channels on them, have to be bonded on top of each other. Dead volumes in practice always appear in the channels, caused by differences in the width of the half-circular channels, or shifts of the wafers during alignment for bonding. The only way to eliminate

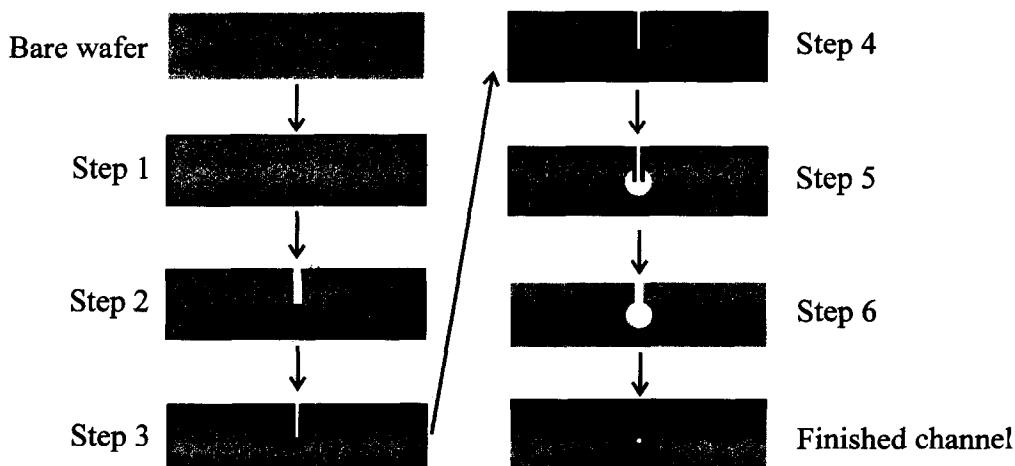


Fig. 5. Outline of the procedure for the etching of buried channels.



Fig. 6. A tubular channel, constructed by bonding two half-tubular isotropically etched channels on top of each other. The channels were etched for half an hour using the solution described in Section 1.3(b).

these problems is to use only one wafer, so that bonding is not necessary. This can be achieved by etching channels beneath the surface of the wafer.

2.2(b) Procedure for making buried channels. The procedure for etching buried channels is outlined in Fig. 5. First the wafer was covered with a thick layer ($3\ \mu\text{m}$) of LPCVD silicon nitride. Then a deep, very narrow trench ($4\ \mu\text{m}$ wide) was etched in the wafer, using RIE etching in a cryogenically cooled RIE with a high energy density source of the Plasma Technology Company [14], using SF_6/O_2 chemistry with a low ion energy [15]. Chromium

was used as the mask material. After etching the chromium was stripped and the wafer was covered with a $500\ \text{nm}$ thick layer of silicon rich, low stress LPCVD silicon nitride ($200\ \text{mTorr}$, 850°C , $70\ \text{sccm}$ dichlorosilane, $18\ \text{sccm}$ NH_3 , $60\ \text{min}$). This nitride also covers the walls and the bottom of the trench conformally. Then the silicon nitride in the bottom of the trench was etched away using a standard RIE system and a SF_6 plasma with a high ion energy and low pressure at 10°C , leaving the bare silicon. The thick layer of silicon nitride on the wafer surface was not etched through. In the



Fig. 7. Buried channels, obtained by etching for 20 minutes in the solution described in Section 1.3(b). The trench is closed using LPCVD silicon nitride.

following steps, the wafer was isotropically etched for 20 minutes using the etching solution described in paragraph 1.3(b). A channel with two strips of nitride sticking into it was formed in the wafer. After etching the wafer was rinsed in de-ionized water to remove the etching solution from the channels. The nitride was removed by etching in 50% HF for two hours, and the wafer was rinsed and dried. In between these steps the wafer was not dried.

The last step consists of the growing of a thick conformal layer on the wafer, that covers the walls of the channel, and also of the trench. The layer is grown so thick that it closes the trench. The materials that can be used for the layer are silicon oxide, silicon nitride, and polysilicon. In our case we used the LPCVD silicon nitride described above. The layer was grown for six hours.

3. RESULTS AND DISCUSSION

3.1 The loading effect

In Table 1 the diameters of the channels in the middle and on the outside of the spiral are given. In Table 1, "outside" means a channel on the outer rim of the spiral, and "inside" means the 15th channel from the rim of the spiral, measured from the outside. The channel is almost in the middle of the column spiral. The diameters shown are average diameters of two places on the wafer (left and right). For each measurement two wafers were used. The overall diameter is the average of all the measurements on the two wafers. The standard deviation σ of the various diameters are also given.

From Table 1 it can be seen that adding extra structures decreases the differences in etch width between the outer and inner channels considerably. Also the standard deviation in the etch widths is

Table 1.
Diameters and standard deviations in the diameters of the etched channels (etch time 30 minutes)

	Diameter outside (μm)	Diameter inside (μm)	σ_{outside} (μm)	σ_{inside} (μm)	Overall diameter (μm)	σ_{overall} (μm)	σ_{overall} (%)
Without extra structures	62	55	3.5	1.4	58	4.3	7.4
With extra structures	44	44	1.9	1.3	44	1.5	3.4

reduced. The average diameters of the channels also decrease, because of the increased depletion of active etching species. The error in the overall etch width decreases from 7.4% without the structures to 3.4% with the structures.

Figure 6 shows a channel obtained with the etching and bonding procedure. This figure reveals one of the problems of this method: when channels with different diameters are bonded together, dead volumes appear. If a coating is applied to the channel wall, it will get thinner in the convex corners and thicker in the concave corners.

3.2 Buried channels

A channel etched using the deep etching technique is shown in Fig. 7. The etch rate depends strongly on the depth of the trench. The shape is not completely circular; it looks like some anisotropic etching has taken place. This phenomenon is also observed by Hashimoto *et al.* [16]. A reason for this phenomenon is discussed by Elwenspoek *et al.* [17]. Because of the depletion of active etching species and/or the accumulation of etching products, the undersaturation of the solution in the channel becomes too low for kinetic roughening (which is the fundamental condition for isotropic etching) and deviations from the isotropic profile appear.

4. CONCLUSIONS

Half-circular, spiral-formed channels for use as a gas chromatography column were etched using the solution described in Section 1.3(b). This solution proved to etch silicon isotropically and leave very smooth walls. Due to the loading effect, channels on the rim of the spiral became larger than the channels on the inside of the spiral. To solve this problem extra structures were placed around the spiral to minimize the local structure density differences between the middle and the rim of the spiral. These reduced the standard deviation in channel width from 7.4% without the structures to 3.4% with the extra structures. The differences in channel width between the channels in the middle and on the rim of the spiral of 7 μm disappeared (etch time 30 minutes).

As a solution to the problems presented by the etching of half-circular channels and then bonding them on top of each other, a method was developed to etch channels beneath the surface of a silicon wafer. This method consists of etching a deep trench in the wafer, covering the walls and the bottom of the trench with silicon nitride, and then removing the nitride in the bottom. After that the silicon is etched isotropically. Then the nitride is removed, and the trench is closed by growing a thick layer of silicon oxide, -nitride or polysilicon on the wafer.

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