A high resolution MEMS based gas chromatography column for the analysis of benzene and toluene gaseous mixtures

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ABSTRACT

his paper reports a high resolution gas chromatography (GC) column based on micro electro mechanical systems (MEMS) technology. This 6.0 m long, 100 μm wide, and 100 μm deep column was fabricated using deep reactive-ion etching (DRIE) to form channels for gas separation, and the channels were sealed with Pyrex 7740 glass by using anode bonding. After the GC column was coated with dimethyl polysiloxane (OV-1) as the stationary phase, benzene and toluene were successfully separated in less than 185 s. The resolution of benzene and toluene was 6.33, which was higher than any previously reported values to our best knowledge. The tailing factors of benzene and toluene were 1.13 and 1.20, respectively, and the number of theoretical plates of toluene was 4850. The system is applicable as a portable device for ambient air quality monitoring and industrial exhaust gas analysis.

1. Introduction

GC systems are used to separate different components of gaseous mixtures, and GCs are important analytical tools for a variety of disciplines, including environmental analysis and pollution management. Martin and Synge [1] invented this method when conducting research on liquid chromatography. However, those traditional GC systems tend to be large, fragile, expensive, and bulky, which makes them unsuitable for on-line and on-site analysis.

In recent years, miniaturized GCs have received increased attention and are under development in several laboratories for the analysis of volatile organic compounds. Chief among these was a micromachined GC system put forward by Terry et al. [2] which consisted of a sample injection valve and a 1.5 m long separating capillary column fabricated on a silicon wafer. The separations of gaseous hydrocarbon mixtures were achieved with the resolution of 1.5, which was not as good as what could be achieved with a standard GC column.

With more recent efforts including that of Potkay et al.'s [3], 3.0 m long, 150 μm wide and 260 μm deep columns were fabricated using a silicon-on-glass dissolved wafer process. The separation of the volatile organic compounds achieved approximately 4900 plates, while the resolving power was not provided in the paper. Reidy et al. and his research team [4–7] fabricated several different columns (e.g., 0.25 m, 1.0 m and 3.0 m in length) using the

silicon-on-glass dissolved wafer process in which the 0.25 m long GC column generated about 1000 plates [4] and the 3.0 m long GC column generated approximately 8000 plates [5] with limited resolution of 1.18 [7].

In addition, although these efforts on miniature GCs have yielded important progress, some key components, such as the interface technology and coating method of the solid phase have not been addressed very well. The interface technology for miniature GCs has not been mentioned before, and the coating method of the stationary phase was not described in detail either.

In this work, a column was designed to obtain substantially higher resolution, with ideal symmetry peaks and high theoretical plates for gas compound separation. Moreover, some key issues including the interface technology and the coating method of the stationary phase were covered in detail.

2. Theory and structure design

If the volume and the concentration of a sample are small enough (about μmol) and in the linear range of adsorption isotherm, the elution curve equation can be determined by Eq. (1) based on the plate theory [8].

$$C = \frac{\sqrt{n}}{\sqrt{2\pi}} \cdot \frac{m}{V_r} \cdot \exp\left[-\frac{n}{2}\left(1 - \frac{V}{V_r}\right)^2\right] \tag{1}$$

where C is the sample concentration at any point of the elution curve, m is the weight of the solute, V is the retention volumn at any point of the elution curve, V_r is the retention volume of the solute, n is the number of theoretical plates. When $V = V_r$, C reaches

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its max value:

$$C_{max} = \frac{\sqrt{n \cdot m}}{\sqrt{2\pi \cdot V_r}} \qquad (2)$$

Derived from the elution curve equation, the number of theoretical plates n can be defined by Eq. (3)

$$n = 5.54(\frac{t_r}{w_{1/2}})^2 \qquad (3)$$

where t_r is the retention time, and $w_{1/2}$ is the width of the peak at half height.

And the theoretical plate height (H) can be determined by:

$$H = \frac{L}{n} \qquad (4)$$

where L is the length of the column. According to the Eq. (3) and (4), as the chromatography peak's bottom width (W) decreases, the number of theoretical plates (n) increases and the theoretical plate heigh (H) decreases accordingly, which results in higher column efficiency. Hence, n and H are the index of column efficiency. Resolution is called overall separation efficiency, which is defined as the difference of retention value between two adjacent chromatography peaks divided by the half of the sum of these two peak's bottom width:

$$R = \frac{t_{r_2} - t_{r_1}}{\frac{1}{2}(W_1 + W_2)} = \frac{2(t_{r_2} - t_{r_1})}{W_1 + W_2} \qquad (5)$$

The definition of resolution (R) in Eq. (5) does not reflect all the factors that influence resolution, because resolution is actually determined by column efficiency (n), selectivity factor (α) and capacity factor (k), hence the resolution also can be described by Eq. (6):

$$R\frac{\sqrt{n}}{4}\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{K}{1 + k}\right) \qquad (6)$$

After the stationary phase is chosen, the selectivity factor could be correspondingly fixed, which means that the resolution is only affected by n. For a column with a certain theoretical plate height, square of the resolution is proportional to the length of column:

$$(\frac{R_1}{R_2})^2 = \frac{n_1}{n_2} = \frac{L_1}{L_2} \qquad (7)$$

Therefore the major approach to improve resolution is to increase the column length. In addition, the uniformity, stability, and thickness of the stationary phase deposited on the channel walls are also important factors affecting the resolution [9,10]. With a chosen stationary phase and a specific dimension, a longer column provides a better peak separation with a higher resolution. However, there is a tradeoff between the separation resolution and the analysis time, since longer columns with smaller cross-sectional areas lead to longer separation time. Hence, in this paper, a 100 μm wide, 100 μm deep and 6.0 m long chromatography column was chosen to obtain the high resolution with acceptable analysis time. A schematic of the design is shown in Fig. 1.

3. Experimental

3.1. Column fabrication

The miniature capillary column was fabricated by etching a 6.0 m long serpentine-shape groove into the surface of a silicon wafer and then hermetically sealing the wafer with a Pyrex glass cover plate. The cross-section of the gas channel was rectangular, with a width of 100 μm and a typical depth of 100 μm. Fabrication of the column proceeded in a sequence of photolithography and etch
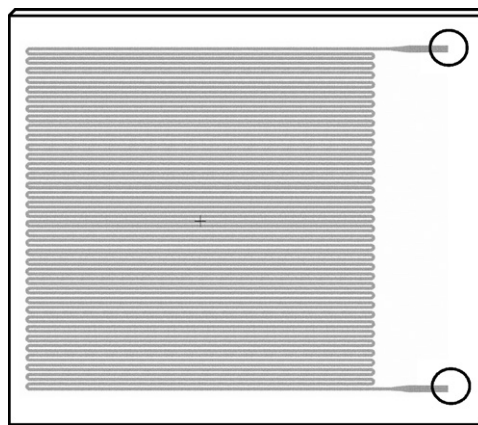

Fig. 1. The schematic diagram of gas chromatography column.

steps (the fabrication process is illustrated in Fig. 2). First, a 2-μm-thick electron-beam evaporation aluminum film was deposited on a p-type ⟨1 0 0⟩ silicon AZ1500 wafer which served as the etch mask in following steps. Second, a thickness of approximately 2 μm photoresist was coated on the wafer and patterned as an etch mask for aluminum. Subsequently, aluminum without the protection of

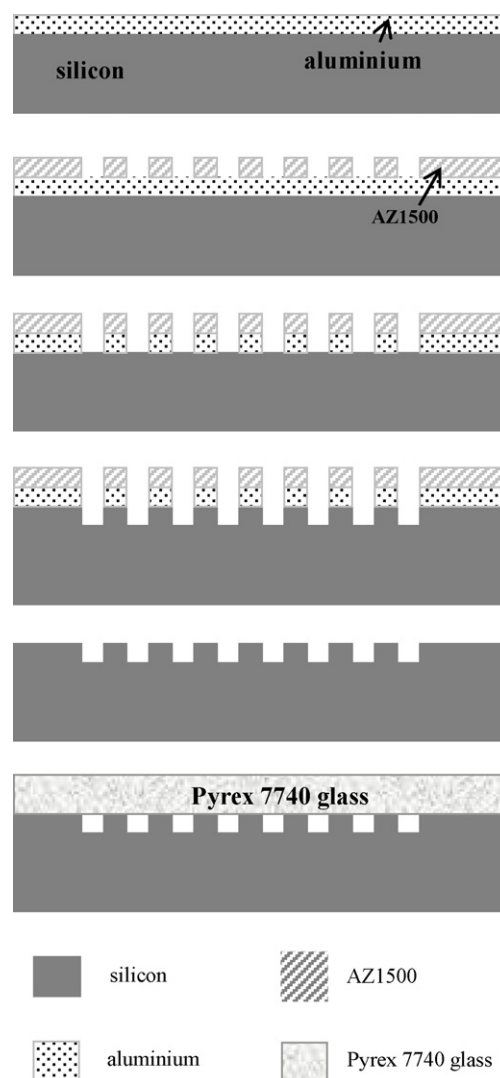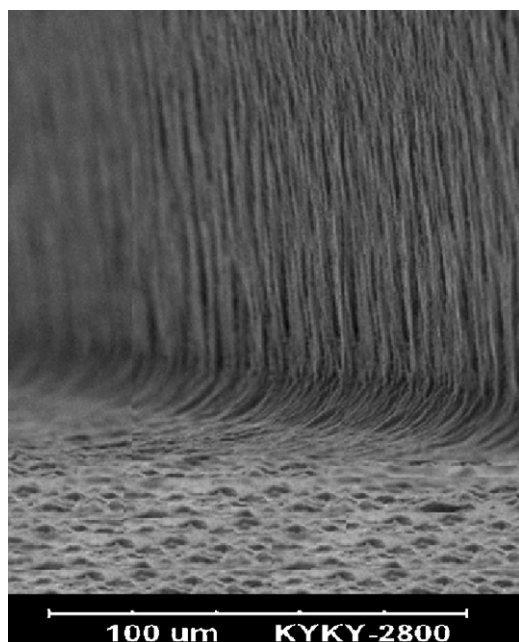Fig. 2. The GC column process flow.

Fig. 3. The SEM view of the channel surface.

Fig. 4. Micromachined Si column, (a) SEM micrograph and (b) complete encapsulated device including the connected base, and the chip dimension is 3.6 cm × 4.6 cm.

photoresist was etched away by an etchant (H_3PO_4) and the silicon surface was exposed. Then, a DRIE process, instead of the anisotropically KOH chemical etching process, was utilized to form the rectangular micro channels. The DRIE process not only made vertical channel walls, but also increased the surface roughness of the channels (see Fig. 3) with 1–2 μm hillocks, which was helpful in enhancing the adhesion strength between the stationary phase films and channel surfaces. In addition, the rough surfaces increased the adhesion area for the stationary phase films. Finally, the aluminum mask was stripped off and a 5 cm Pyrex 7740 glass plate was anodically bonded to the silicon wafer.

3.2. Interface technology

The inlet/outlet interface technology of MEMS based GC columns is a key factor. If not properly tackled, some problems, such as instability of the interface, air leakage from the interface and the airflow jamming would happen, which usually led to the failure of the GC columns. In order to solve these problems, a fixed base (the base dimensions is 8.0 mm long, 4.0 mm wide and 5.0 mm high.) was used to connect the tubes with the inlet and the outlet of the column. The major steps are briefly covered: First, a film of heat-resistant adhesive (the brand and the type of the heat-resistant adhesive were Vabond and VE-3240, respectively) was coated on the bottom surface of the base, and then the base was aligned with the inlet and the outlet carefullly and bonded with the column; After 30 min, more heat-resistant adhesive was coated around the base with a steel tube (Tubing, steel, 1/32 in. × 0.25 nm^{ID})into the base, and then some heat-resistant adhesives were coated around the joint points; Subsequently, the column was tested under vibration using a KQ-500DB ultrasonic cleaning machine with 80% power for an hour without showing any looseness. In addition, a burst pressure test with 0.4 MPa pressure was applied on the column and the interface remained undamaged. Fig. 4 shows a photograph of the completed GC column including the connected base (the chip dimension is 3.6 cm × 4.6 cm).

3.3. The stationary phase coating

The uniformity, stability and thickness of the stationary phase film are important factors that can affect the separation efficiency.
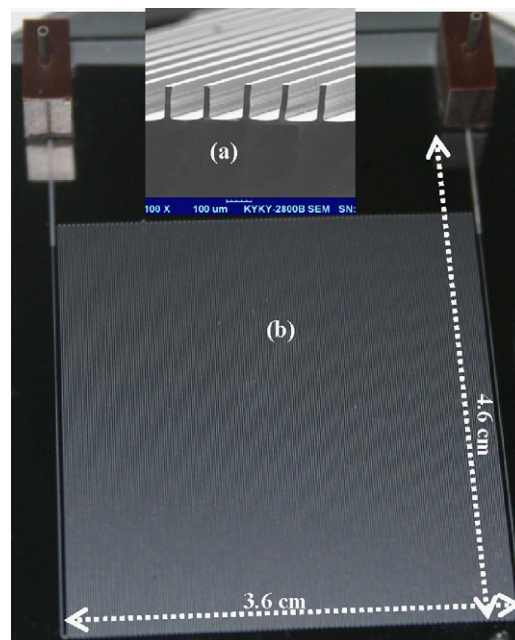
In this work, a dynamic coating procedure was used, in which about 5 μL dimethyl polysiloxane (OV-1, the molecular formula is $C_3H_9OSi\cdot(C_2H_6OSi)n\cdot C_3H_9Si$) was dissolved in 2.0 mL mixtures of n-pentane and dichloromethane with a volume ratio of 1:1. The mixture was agitated for 30 min to ensure full dissolution. The inlet of the column was connected with a capillary, and the outlet was connected with a laboratory made micro-pump, which was used to inject the stationary phase solution into the GC column. After the GC column was full of the solution, the micro-pump was turned off for 30 min to make sure that it was long enough for the stationary phase to attach to the channel wall. Then, nitrogen gas was delivered through the column for a few hours to completely evaporate the n-Pentane and dichloromethane. Subsequently, the column was put into an oven under a nitrogen atmosphere in which the temperature of the oven was first increased gradually by 5 °C/min until 100 °C and then the temperature of the oven was kept at 100 °C for 4 h. Fig. 5 shows an SEM view of the stationary phase film coated on the column wall, in which the film is uniform and adheres well to the channel. The composition analysis of the film, by X-ray photoelectron spectroscopy, is described in Table 1 which shows that
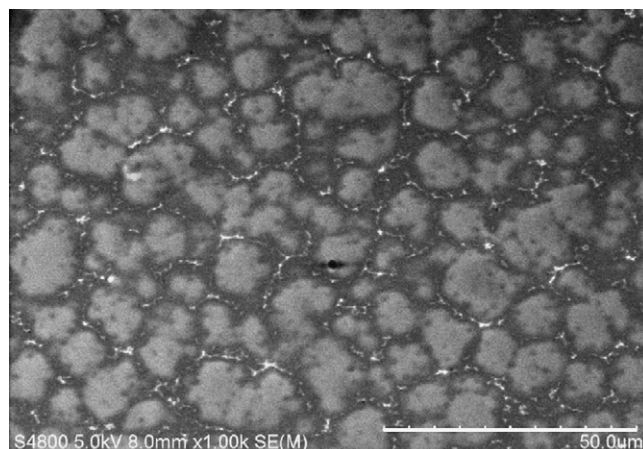

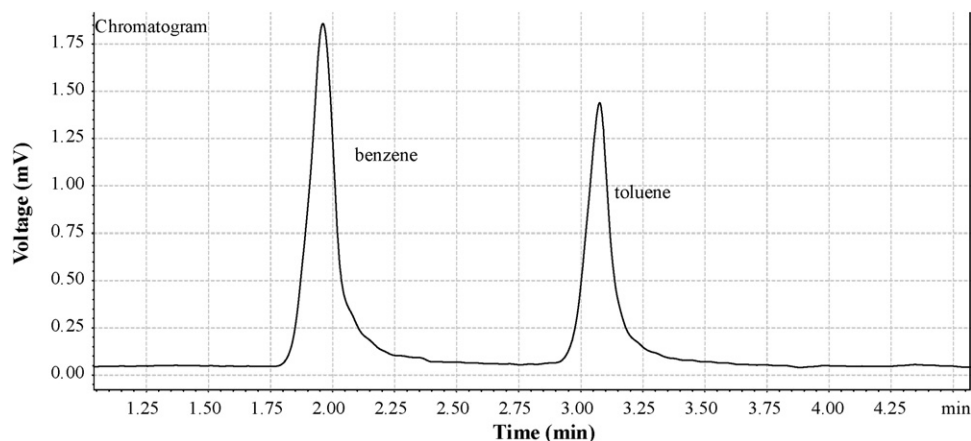**Fig. 5.** The SEM view of the stationary phase film.

Fig. 6. The separate curve of 6.0 m long GC column. The left chromatographic peak is the benzene and the right chromatographic peak is toluene.

Table 1
The composition analysis of the film, by X-ray photoelectron spectroscopy, is described in this table which asserts the composition element agrees with the composition of OV-1 (the molecular formula is $C_3H_9OSi\cdot(C_2H_6OSi)n\cdot C_3H_9Si$).

Composition element	C	Si	O
Atom percentage	53.69	24.07	21.86
Weight percent	38.17	40.10	20.70

the composition agrees with the composition of OV-1. In addition, several different positions of the film were chosen for analysis with consistent results.

4. Results and discussions

GC performances were measured through the flame ionization detector (FID) method on a Shimazu GC-2010 GC system. In the test, the operating temperature of columns was 25 °C and the carrier gas was helium. The samples were mixtures of benzene and toluene, which were injected via a dual channel Qc-2 gas sampler at time zero. The sample volume was 5 μL; the top-air method was used with a split ratio of 1:500. The column was operated at the optimal flow rate of 100 mL/min. The chromatogram graph is shown in Fig. 6, wherein the left peak is benzene, and the right peak is toluene.

The chromatogram shows that the retention time of benzene was 117.6 s, and the retention time of toluene was 184.8 s. The half-peak widths of benzene and toluene were 5.88 s and 6.24 s, respectively. From the resolution Eq. (5), the resolution of benzene and toluene was computed as 6.33, and the separation of the gas mixture was very ideal. The chromatogram also shows that the tailing factors, which show the peak tailing, of benzene and the toluene, were 1.13 and 1.20, respectively, both of which were close to the theoretical value 1.0. Hence the gas chromatography peaked symmetrically. Moreover, the GC column generated approximate 4850 theoretical plates which already reached the previously reported level. Hence we concluded that the column separated the benzene and toluene with the desirable separation performance. The resolution and the number of theoretical plates in several tests were nearly the same with symmetric peaks. Furthermore, these results verified that the elution phenomena of the stationary phase film did not show up, which further demonstrated the sound coating effect of the stationary phase.

5. Conclusions

This paper demonstrated the structure design, theoretical analysis, fabrication, and experimental results for a microfabricated

gas chromatography column that successfully separated benzene and toluene using helium as a carrier gas. Additionally some key issues such as the interface problems were tackled properly and the stationary phase was coated evenly and adhered very well to the columns. The experimental results showed that the resolution of benzene and toluene was 6.33, which was higher than what had been reported in the past. The tailing factors of benzene and the toluene were 1.13 and 1.20, respectively, close to the theoretical value 1, which showed that the gas chromatography peaked symmetrically. Moreover, the GC column generated approximately 4850 theoretical plates which were comparable to the previously reported level. Potential applications include ambient air quality monitors, on-line and on-site industrial exhaust gas analysis, and methane gas probes.

References

[1] A.J.P. Martin, R.L.M. Synge, A new form of chromatogram employing two liquid phase, Biochem. J. 35 (1941) 1358–1368.
[2] S.C. Terry, J.H. Jerman, J.B. Angell, A gas chromatographic air analyzer fabricated on a silicon wafer, IEEE Trans. Electron. Dev. 26 (1979) 1880–1886.
[3] J.A. Potkay, J.A. Driscoll, M. Agah, R.D. Sacks, K.D. Wise, A high-performance microfabricated gas chromatography column, in: Proceedings of the Sixteenth Annual IEEE Conference on Micro Electro Mechanical Systems (MEMS), January, Kyoto, Japan, 2003, pp. 395–398.
[4] S. Reidy, G. Don, M. Agah, R. Sacks, Temperature-programmed GC using silicon microfabricated columns with integrated heaters and temperature sensors, Anal. Chem. 79 (7) (2007) 2911–2917.
[5] M. Agah, J.A. Potkay, G. Lambertus, R. Sacks, K.D. Wise, High-performance temperature -programmed microfabricated gas chromatography columns, IEEE J. Microelectromech. Syst. 14 (5) (2005) 1039–1050.
[6] G.R. Lambertus, C.S. Fix, S.M. Reidy, R.A. Miller, D. Wheeler, E. Nazaro, R. Sacks, Silicon, microfabricated column with microfabricated differential mobility spectrometerfor GC analysis of volatile organic compounds, Anal. Chem. 77 (2005) 7563–7571.
[7] G. Lambertus, A. Elstro, K. Sensenig, J. Potkay, M. Agah, S. Scheuering, K. Wise, F. Dorman, R. Sacks, Design fabrication and evaluation of microfabricated columns for gas chromatography, Anal. Chem. 76 (2004) 2629–2637.
[8] J.A. Jónsson, Chromatographic Theory and Basic Principles, Marcel Dekker, New York, 1987, p. 50.
[9] C.F. Poole, S.K. Poole, Characterization of solvent properties of gas chromatographic liquid phases, Chem. Rev. 89 (1989) 377–382.
[10] A. Bhushan, System Optimization for Realizing a Miniaturized Gas Chromatograph Sensor for Rapid Chemical Analysis, LSU, Baton Rouge, LA, December, 2006, p. 103.

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