A LOW-POWER PRESSURE- AND TEMPERATURE-PROGRAMMABLE μ GC COLUMN

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ABSTRACT

This paper presents the theory, fabrication and experimental results for the highest performance, low-power micro gas chromatography (μ GC) column realized to date. The suspended-dielectric 1m-long column is split into two sections, permitting pressure programming. Furthermore, each section is individually temperature programmable. The integrated heaters have a mean resistance of 6.8 k Ω and a TCR of 1439 ppm/ $^{\circ}$ C. A single heater in the fully suspended column requires 6 mW to raise the local column temperature by 100 $^{\circ}$ C in vacuum (10 μ Torr). The column has separated 10 alkanes in 52 s and four chemical warfare agent simulants and an explosive simulant in 60s.

INTRODUCTION

Accurate chemical (gas) sensing is critically needed for a wide variety of applications, including those in industrial process control, food processing/monitoring, environmental monitoring, pharmaceutical screenings, health care, and homeland security. However, past devices have often lacked speed, sensitivity, stability, and, in particular, selectivity. A miniaturized gas chromatograph (GC) potentially provides a solution to all of these problems, especially selectivity, since it is able to separate components in space and time.

In a typical gas chromatography system, the separation process begins when a gaseous sample is injected into a separation channel (column). The column is usually coated with a thin film, known as the stationary phase, which enhances the separation ability of the column and can be chosen based on the targeted compounds. As a carrier gas transports the sample through the column, the individual components in the mixture spend different amounts of time adsorbed in the stationary phase on the wall of the column. This adsorption process is dependent on several variables, including the component vapor pressures and their polarities, the column temperature, the carrier gas velocity, the stationary phase characteristics, and the component retention factors. In general, compounds that spend less time in the stationary phase exit the end of the column first, where they are detected. Thus, the elution time can be used to identify the compound, and the magnitude of the detector signal can be used to determine its concentration.

Commercial GC systems exist, but are inconvenient in field use due to their size and power. In some cases, gas samples are collected in the field and analyzed in the laboratory using a conventional GC, but this process is inefficient at best. By miniaturizing such systems, lower power levels may be achieved, facilitating analysis directly in the field. The addition of integrated pre-concentrators to such miniaturized microsystems could also aid in reducing analysis time relative to commercial systems.

The first efforts to produce a μ GC began in 1970 at Stanford University [1], with more recent efforts at Lawrence Livermore [2] and Sandia National Laboratories [3]. Various column structures have been explored, including anodically-bonded glass-silicon columns [2,3,4], silicon/silicon dioxide fusion-bonded columns [5], metal LIGA-based columns [5], and parylene columns [6]. Although these efforts have yielded important progress, they have not yet provided the high performance and low-power operation needed for many applications. In addition, none of the systems

Figure 1. Drawing of the CVD column structure.

developed to date have been completely miniaturized or fully integrated.

The column described here is aimed at substantially lower power, smaller size, and higher performance than anything reported in the past. It leverages previous work at Michigan on column design [4], coating and testing [8], and process technology [9]. It forms the heart of a μ GC intended for an environment monitoring system that is currently under development as part of the NSF-funded Engineering Center for Wireless Integrated MicroSystems (NSF WIMS ERC). This microsystem, which will monitor temperature, pressure, humidity, and gas composition with part-per-billion sensitivity, is targeted at less than 5cc with an average power of less than 1mW. The finished system will analyze 30+ volatile organic compounds (VOC's) in less than 5 mins. The following sections describe the theory, fabrication, and experimental results for the column portion of this microsystem.

THEORY AND DESIGN

The column structure is shown in Fig. 1 and is designed to minimize power and maximize performance. As shown, the column is suspended and vacuum-sealed to reduce conductive and convective heat losses, etched back to improve the thermal response time, and coated with metal to decrease radiation losses and improve temperature uniformity across the column. The structure consists of two individually-suspended and heated columns so that the first column may be bypassed (in order to increase flow in the second column) using integrated microvalves. Thus, the column has two zones, both temperature and pressure programmable. As μ GC columns decrease in size, their resolution also decreases; temperature and pressure programming provide a powerful means to increase performance. The column is made up of semi-circular channels, which were chosen for ease in processing and to minimize stationary phase pooling. In general, circular-cross-section channels perform well over a larger range of flow than other column shapes, permitting increased system design flexibility.

The performance of gas chromatography columns is conventionally measured in terms of the total number of theoretical plates (N) (a measure of the resolving power of the column) and in terms of the height equivalent to a theoretical plate (H) (a measure of the efficiency of the column). Golay performed the first analytical modeling of gas chromatography channels in 1958 [10]. The H of a column with a circular cross section is given by:

$$H = 2 \frac{D_g}{u} + \frac{1 + 6k + 11k^2}{96(1 + k)^2} \frac{ud^2}{D_g} + \frac{2h^2ku}{3D_i(1 + k)^2}, \quad (1)$$

Figure 2. Effect of the channel diameter and length on the theoretical flow rate of the column.

where D_g and D_l are the diffusion coefficients in the gas and liquid phases, respectively, k is the retention factor, h is the thickness of the liquid phase, and d is the channel diameter. The average carrier gas velocity, u , is given by (2), where u_o is the outlet gas velocity, f_2 is the Martin-James gas compression correction factor, given in (3), p_o is the outlet pressure, p_i is the inlet pressure, and L is the column length.

$$u = u_o f_2 = \frac{d^2 p_o \left(\left(\frac{p_i}{p_o} \right)^2 - 1 \right)}{64 \eta L} f_2 \quad (2)$$

$$f_2 = \frac{3 \left(\left(\frac{p_i}{p_o} \right)^2 - 1 \right)}{2 \left(\left(\frac{p_i}{p_o} \right)^3 - 1 \right)} \quad (3)$$

To determine the total resolving power of a column, the total number of plates, N , is calculated as

$$N = \frac{L}{H}, \quad (4)$$

where L is the total length of the column. Finally, the holdup time, t_m , is the time it takes for an unretained component to be injected into the system and travel through the column to the detector. It is calculated as in (5):

$$t_m = \frac{L}{u} \quad (5)$$

For the μ GC under development, many factors constrain the design and performance of the column. Integration with a MEMS vacuum pump further facilitates miniaturization and low-power operation, but hinders the ability to increase the performance of the column by increasing its inlet pressure as is conventionally done. The use of air as a carrier gas eliminates the need for gas storage and facilitates miniaturization. However, air has a higher viscosity and smaller diffusion constant than conventional carrier gases such as hydrogen, resulting in a diminished flow rate in (2) and decreased resolving power in (4). In addition, the total analysis time was limited to less than 10min, and because of fabrication and power issues, the diameter of the low-mass columns was limited to between 50 μ m and 120 μ m. Total length was limited to 4m.

The plots shown in Figs. 2 and 3 were generated using (1-5) and show the tradeoff between various design parameters. Figure 2 shows the column flow rate for various channel dimensions. Although a low flow rate is preferable for the MEMS vacuum pump (less than 2sccm at 0.5atm of pressure), a high flow rate is favorable for sweeping components out of the preconcentrator and across the detector. However, other techniques can also be applied, such as split flow injection to improve the gas flow rate over the preconcentrator and detector. Thus, flow should be

Figure 3. Effect of the channel diameter and length on the theoretical resolving power of the column.

maximized while remaining within the requirements of the vacuum pump.

Figure 3 displays the relationship between the resolving power of the column and its diameter and length. There is an optimum column diameter for each length (for a fixed differential pressure). Based on fabrication and power considerations, it is desirable to keep the column diameter and length small. However, a high resolving power is required to be able to separation all of the components in a complex mixture of 30+ VOC's. Thus, a column diameter of around 90 μ m and lengths of 0.5m, 1m, and 2m were chosen as a compromise among all of the system requirements. Nearly all of the data points of interest correspond to a total analysis time of less than 5 minutes, assuming a maximum retention factor of 10.

Figure 4. Thermal model and the equivalent circuit for the suspended CVD column.

Figure 5. Power loss as a function of pressure for a 0.5 m column suspended at 4 points using the model in Fig. 4. The model predicts a power consumption of 14 mW in vacuum.

Next, a thermal model of the device was developed to optimize the device speed and power and predict its behavior. The model in Fig. 4 considers the effects of conduction (through the supports and air), convection and radiation. Conduction occurs both through the oxynitride supports and through the air above and below the column. Conduction through the supports was modeled assuming a thermal conductivity of 1.4 W/mK for the oxynitride. The thermal conductivity of air between two enclosed plates is a function of pressure, approximated in [11] by:

$$k_{air} = k_{air,0} \times \frac{1}{1 + \frac{7.6 \times 10^{-5}}{P \times d / T}} \quad (6)$$

where $k_{air,0}$ is the thermal conductivity of air at room temperature and pressure (0.0284 W/mK), P is the pressure, d is the distance between the plates and T is the average temperature of the plates.

Due to the transparency of the dielectric column, radiation occurs from both the column top and bottom in an enclosed space. In both cases, heat loss can be modeled as [12]:

$$Q_{rad} = \frac{\sigma_{SB} A (T_{S1}^4 - T_{S2}^4)}{\epsilon_{S1}^{-1} + \epsilon_{S2}^{-1} - 1} \quad (7)$$

where σ_{SB} is the Boltzmann constant, A is the area, and T_{S1} and T_{S2} and ϵ_{S1} and ϵ_{S2} are the temperatures and emissivities of the two surfaces, respectively. Due to the size of the cavity, viscous forces in the air are much larger than buoyancy forces and no fluid motion occurs. Thus, the Rayleigh number is very small and convection can be neglected [13].

The plot in Fig. 5 was generated using (6), (7) and Fig. 4. It predicts the heat loss as a function of pressure for the column. In vacuum, the model predicts a heat loss of 14mW at a temperature rise of 100 °C.

FABRICATION

Fabrication of the column (Fig. 6) requires 6 masks. First, a grid is anisotropically etched in a 2 μ m-thick PECVD oxynitride dielectric layer using a reactive ion etch (RIE). A vertical sidewall is necessary in order to prevent voids when the channel is later sealed and, thus, improve the strength of the column. The grid is then undercut using a 25 minute long dry isotropic etch and sealed using a 12 μ m-thick PECVD oxynitride layer (Fig. 7). Both oxynitride layers are designed to be stress free and require less than 15min for deposition.

Next, a 200/400Å Ti/Pt metal layer is deposited and patterned to form the heaters and temperature sensors. The Ti/Pt layer is also used to reduce radiation losses and increase temperature uniformity across the column. Next, the Ti/Pt layer is protected with another 2 μ m-thick oxynitride layer and then a 300/1000/5000Å Ti/Pt/Au bond ring is deposited via evaporation. The intermediate platinum layer serves as a diffusion barrier during the later bonding step. Finally, the oxynitride is wet etched for device isolation and to open metal contacts. The cap wafer requires 3 additional masks. Two DRIE etches form a recess and low-dead-volume fluidic connectors, and a 300Å/4 μ m Cr/Au bond ring is plated. Finally, the two wafers are bonded together utilizing Si/Au eutectic formation, and a dry etch is used to release the device (Fig. 8). Stress minimization of both the metal and oxynitride films is critical to device release. In addition, low-dead-volume fluidic interconnects are crucial in preventing band broadening. It should be noted that the structure in Fig. 5(d) contains a dielectric layer connecting the column to the substrate. This layer is used for structural support; however, it may optionally be etched away to fully suspend the device and reduce its power consumption. The process can also be extended by

Figure 6. Process flow for the released dielectric columns.

Figure 7. Cross section of a sealed buried channel with a height of 72 μ m, width of 97 μ m, and ceiling thickness of 15 μ m.

Figure 8. SEM of the bottom side of a released column. A picture of the backside of the transparent dielectric column is shown (inset). The heater is visible through the column.

bonding a second cap wafer to the bottom of the device and, thus, vacuum encapsulating the column.

RESULTS

A fabricated 1m column is shown in Fig. 9. The three low-dead-volume fluidic interconnections are visible on the top substrate and permit individual coating of the two column segments and pressure programming. The electrical interconnects can be seen on the shelf along the bottom of the column and provide contacts to the heaters, temperature sensors and substrate.

After fabrication, initial tests were done to examine the strength of the eutectic bond and its hermeticity. First, a gross bond strength test was completed by prying apart the two wafers using a razor blade. The bond area was extremely hard to break, and when it did, the breaking occurred in the substrate and not along the bond interface. Next, capillary tubing was epoxied into the fluidic connectors and fluidic pressure of up to 0.5atm was applied to the input. The device was immersed in acetone and no leaks were visible, verifying the gross hermeticity of the bond and viability of the fluidic interconnections. Complete characterization of a similar bond technology can be found elsewhere [14]. The current bond technology differs from [14] in that it utilizes metal feedthroughs and a PECVD isolation layer.

Next, the device was placed in an environmental oven and the temperature was varied from 25°C to 125°C. The resistances of the temperature sensors were found to have a mean resistance of 6.88 k Ω and a TCR of 1439 ppm/°C. The devices were then placed in a custom vacuum chamber at 10 μ Torr. Power was applied to a single heater in a fully suspended column and only 6 mW was required to raise the local column temperature by 100°C. The devices were then coated with a PDMS stationary phase. During coating, the devices withstand an inlet pressure of 25psi without damage. Next, the device was hooked up to an injection system and flame ionization detector (FID). The separation of 10 alkanes in 52s is shown in Fig. 10. The separation of four chemical warfare agent simulants and an explosive simulant in 60s is shown in Fig. 11. Both separations utilized a temperature ramp from of 30 to 100°C at 50 °C/min.

CONCLUSION

This paper presented a high-performance low-power μ GC column operating at milliwatt power levels and capable of separating 10 alkanes in under 52 s. Such columns are critically needed for remote chemical monitoring systems for homeland security, environmental monitoring and health care.

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Figure 9. Picture of a finished 1 m column next to a dime.

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Figure 10. Separation 10 components in 52s using the 1 m column. A temperature program of 30-100°C at 50°C/min was used in conjunction with a flame ionization detector.

Figure 11. Separation of 4 CWA simulants and an explosive simulant in 60s utilizing the 1 m column. A temperature program of 30-100°C at 50°C/min was used in conjunction with a flame ionization detector.