Micro-Fabrication of All Silicon 3 Meter GC Columns Using Gold Eutectic Fusion Bonding

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This work highlights a new bonding technique for micro-fabrication of an all silicon 3 meter gas chromatography column that could withstand the temperature cycling required for axial temperature programming. Proper separation of a complex gas mixture using a miniaturized GC column is critical in improving the overall performance of a lab on a chip system for environmental monitoring, medical diagnoses, and gas impurity measurement. To improve upon current methodology the column was first fabricated using micro-fabrication processes; experimentally validated using a high performance 3 meter GC column coated with OV-1 stationary phase. This process demonstrates that the bonding quality of the GC column to a 200 μm thick silicon lid was improved when using a new gold eutectic bonding technique. Furthermore, a new quality control technique was developed in order to test the overall bonding quality of the bonded pieces by fixing the bottom column and applying a mechanical shear force to the top lid. This method could ultimately be used for quality control of each individual bonded columns. The gold bonded interface of the gold diffusion bonded area is further characterized using surface analysis. In the end, the utility of the column was demonstrated by separating 21 organic compounds with different Kovats retention index and molecular weights in less than five minutes.

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Manuscript submitted April 8, 2015; revised manuscript received June 26, 2015. Published July 15, 2015. This paper is part of the JSS Focus Issue on Micro-Nano Systems in Health Care and Environmental Monitoring.

There has been considerable interest in miniaturizing the gas chromatography column system since its introduction by Terry in 1970 and subsequent efforts by Reston and Kolesar in 1990. Sandia National Lab was the first to integrate a MEMS GC column with chemical sensor arrays and a preconcentrator into a hybrid system for fast detection of specific explosive markers and trace organic compounds in environmental samples. Chia-Juang Lu developed the first-generation hybrid MEMS gas chromatograph system which uses air as the carrier gas and a silicon etched column sealed with glass anodic bonding. Also recently Garg has developed a compact mini-GC system for detection of hazardous pollutants in environmental air samples. However, these systems are selective and the heating system are not ideal. Despite significant progress by Enose to integrate all the components of a micro-GC system, currently there is no fully integrated, portable, low power, and low cost GC system capable of separating and detecting multiple VOCs in a short time.

GC columns are the heart of the GC system where separation takes place; therefore, properly sealing a micromachined GC column is critical in systems integration thus improving the overall performance. There are several techniques that have been developed for proper bonding and sealing of MEMS micro-GC columns such as anodic bonding, gold eutectic bonding, and fusion bonding. Anodic bonding is a well-established bonding technique for properly sealing of micro-channels columns and currently accounts for packaging the majority of the silicon microfabricated GC columns. Among the many bonding methods available for bonding a high density micro-machined surface, anodic bonding is possibly the one with the lowest capital cost, while offering a strong bond. However, its main disadvantage for the micro-GC column is the necessity of bonding silicon to a material with sufficiently different thermal conductivity such as Pyrex glass. High frequency temperature cycling of a GC column comprised of two materials with different thermal expansion coefficients and thermal conductivities enhances fatigue cracking, reduces fatigue life, and influences non-uniformity in the temperature profile. As a result, anodic bonding of a Pyrex glass lid to a micromachined silicon column reduces the overall column efficiency while it requires additional power to reach a steady-state temperature.

Fusion bonding, while an easy and low cost bonding technique, presents many challenges due to the rough surfaces of the micro machined GC column. The rough metrology of the micromachined surfaces enhances formation of small voids and gaps between the two bonding pieces. Previously, our attempts to perform direct silicon-silicon bonding without an intermediate layer have failed. We observed only the partial bonding of silicon, which was mainly due to the high roughness and contamination on the surface of the column. Finally, the gold eutectic bonding as a standalone method does not create a durable bond to withstand the high pressure condition needed for GC column operation. Even though all these techniques are available for packaging a GC column, none of these techniques are ideal for bonding a high density micro-machined surface.

This paper introduces a novel bonding technique for micro-fabrication of all silicon 3 meter gas chromatography columns. The bonding technique enables sealing of a GC column that withstand the temperature cycling and decrease degradation over time. This method eliminates the need for anodic bonding and provides a better temperature uniformity when operates at a higher temperature.

To improve the bonding quality, we performed a two-step process: First, the two pieces were bonded temporary using gold eutectic bonding at the eutectic temperature of the gold, followed by the annealing step by placing the pre-bonded column in a furnace at 1200°C for two hours. The bonding strength was then quantified by connecting the GC column to a compressed nitrogen system with a controlled bleed to an ambient valve. The quality of the bond interface was further characterized using SEM/EDX imaging. Finally, a new bonding quality control test was developed by measuring the displacement of the bonded column while applying a mechanical shear force to the column.

Fabrication Process

The microfabrication of the column started with a 4 inch diameter P doped silicon wafer (0.5–0.42 Ohm-cm 500–550 μm SSP prime
Grade). Megaposit SPR 220 photoresist was spin-coated on the wafer at 2000 rpm for 50 seconds. The photoresist thickness was measured using Nanospect reflectometer to be around 10 μm. Following the baking step of 3 minutes at 120°C, the wafer was lithographically exposed in order to print the inlets and aligner marks on the back side of the wafer. STS HRM Deep Ion Reaction Etching (DIRE) was used to etch 300 μm deep holes half way anisotropically in silicon. During the DIRE process, SF₆ and C₄F₈ were used for etching and passivation layer deposition respectively. The resist layer was removed using acetone, and the wafer was cleaned in the piranha solution for 20 min. The same resist coating procedure was repeated on the topside of the wafer. Next, a 400 nm thermal oxide mask layer was thermally grown using a Tystar nitride furnace. The column pattern was transferred to the top of the wafer using the back side alignment technique. Mask aligner aligns the inlet of the columns with the 200 μm in the diameter inlet port holes etched in the previous steps. The oxide mask layer was removed using the BOE 6:1 wet etch process. This step was essential to expose the channels. DRIE was used again to etch 300 μm deep channels on the topside of the wafer and to etch the holes all the way through. The resist layer was then removed using acetone. A thin layer of silicon oxide was grown thermally and subsequently removed by buffered oxide etch (BOE) to reduce their surfaces roughness inside the channel. Reducing the channel roughness is important to ensure formation of uniform stationary phase coatings. The wafer was diced and rinsed with DI water.

A double sided polished 4 inch dia. P doped silicon wafer (0.5–0.42 Ohm-cm 200–225 μm SSP prime Grade) was used to seal the column. Denton Explorer was used to deposit 10 nm of Ti as an adhesion layer subsequently 100 nm of gold was deposited. The wafer was diced to match the exact dimensions of the previous fabricated chips. Both the silicon column and the lid were cleaned in piranha solution for 20 minutes at 120°C and subsequently immersed in BOE solution for 2 min to remove the native oxide. The dies were rinsed with DI water for 5 minutes and nitrogen blow-dried. The two dies were brought into contact with a minute of drying, then were placed inside Karl Suss SB6 wafer bonding tool. The tool’s temperature and pressure were set to 420°C and 10 MPa respectively.

The bonded die were annealed at 1200°C (Tystar furnace: 2500 sccm N₂, 2 hours) for two hours to ensure gold atoms diffuse into the silicon and form a gold silicon alloy. Formation of the gold silicon alloy improves the bonding strength and reduces the stress. Next, the columns were coated with (Ohio Valley) OV-1 stationary phase. Static and dynamic coating techniques were attempted. Static coating is the standard coating technique for coating the commercial GC columns mainly due to its good coating uniformity. In static coating, a column is filled with a dilute solution of stationary phase in a suitable solvent. One end of the column is sealed to control the evaporation of the solvent, and the vacuum is applied to the other end of the column to form a uniform stationary phase coating on the inner wall of the column. The thickness of the stationary phase was calculated based on the viscosity of coating solution to be around 3 μm.

Dynamic coating of the GC column was also attempted at different concentrations, 0.1, 2, and 5% (weight to volume) in toluene. First the column was filled with the stationary phase solution, and the excessive solution was removed by pressurizing the column at 40 psi for 2 minutes. Next, the pressure was reduced to 0.2 psi and the column was left to dry at 120°C overnight. In this work we present the data for 5% (W/V) OV-1 coating. Figure 1 shows the fabrication process flow of all silicon micro-GC column.

The inlet of the GC column was connected to a 250 μm diameter fused silica (FS) capillary via NanoPort fitting. The NanoPort fitting was aligned with the inlet hole on the chip and cured in a convection oven at 350°C for an hour. The outlet was connected to the same diameter fused silica by inserting the capillary into the pocket that was etched in silicon. The capillary was attached and sealed using Miller-Stephenson epoxy 907 adhesive. Figure 2 shows the schematic of a 3 meter GC MEMS column.

Figure 1. Process flow for fabrication of all silicon micro-GC column: (A) 500 μm (100) silicon wafer; (B) Resist spin coating; (C) Channel lithography; (D) STS HRM Deep RIE; (E) Resist striping; (F) Back side resist spin-coating; (G) Alignment and lithography; (H) Deep IRE of input hole; (I) Resist striping; and (J) 200 nm gold deposition on a wafer and wafer bonding.

Figure 2. (A) Schematic of 2 and 3 meter GC column, (B) 3 meter MEMS GC column, and (C) etch profile of the column.

Results and Discussion

The bonding strength was quantified by connecting the GC column to a compressed nitrogen system with a controlled bleed to ambient valve. The pressure in the column was controlled by the flow rate of the bleeding gas into the column and a pressure transducer was integrated to measure the pressure difference. The gold eutectic fusion bonded column demonstrated sealing up to 90 psi compared to the gold eutectic bonded column which failed at 40 psi. Furthermore, the bonding strength was tested by insertion of a flat tweezer between the bonded pieces. The gap between the two pieces of gold eutectic fusion bonded was small enough to prevent insertion of the tweezer. Finally, the quality of the bond interface was characterized using SEM imaging. The SEMs images presented in Figure 3 show formation of a continuous silicon interface.

The bonding interface of the micro-column was further analyzed using SEM/EDX Zeiss to study the bond formation and micro-voids characterization. The area 1 boxed in Figure 4 shows the gold eutectic bonding area and area 2 is silicon. These voids are suspected to be the gold-silicon composite alloy. The heat-treatment profile affects the diffusion rate and densification, as well as residual stress.
development in the bonding area. The diffusion coefficient of gold in silicon is reported to be $1.1 \times 10^{-7}$ and the diffusivity and solubility of gold into silicon increase at higher temperature. Therefore, at higher temperature a thicker layer of gold silicon alloy forms and a stronger eutectic bond is expected. Temperature and processing time are the key factors that affect the quality of the eutectic bond. High amount of energy is needed for atoms to overcome the diffusion boundary and form a strong gold-silicon bond. Therefore, at higher temperatures, gold atoms have sufficient energy to diffuse into silicon and form an alloy.

Furthermore, a die shear test was conducted to evaluate the bonding strength. A 22 mm by 22 mm column die was diced into sixteen 3.5 mm by 3.5 mm pieces. Dage 4000 was used to perform the die shear test using a 100 kg cartridge. Figure 5 shows the die shear test experimental setup and the direction of the applied shear force. The shear height and speed were set at 100 μm and 100 μm/s respectively. Table I summarizes the experimental parameters.

The maximum mechanical shear load for each sample was measured and plotted in Figure 6. The average shear strength of seven samples is 4.67 MPa, which is adequate to the standard GC operating pressure range. The average shear strength of the gold eutectic bonded GC column was much lower than the column bonded by previously reported fusion bonding and fusion-eutectic bonding. This was due to

![Figure 4. a) SEM images of the bonded interface of gold eutectic bonded; b) Energy dispersive X-ray showing the Au richness around the bonded area; c) Location of gold atoms at the interface; d) Location of silicon atoms; e) Location of oxygen.](image)

![Figure 5. Die Shear Test setup.](image)

![Figure 6. Shear test results of seven samples.](image)

| Table 1. Shear Test Parameters. |
|----------------------------------|
| Cartridge DS 100 KG             | Range 100 kg                   |
| Sample Size                     | 3.5 mm × 3.5 mm                |
| Shear height                    | 100 μm                        |
| Shear Speed                     | 75 μm/s                       |
Table II. Shear Test Results.

| Shear Test results |          |
|--------------------|----------|
| Average            | 4.67 MPa |
| Standard deviation | 0.69 MPa |
| Max                | 5.71 MPa |
| Min                | 3.59 MPa |
| Number of Samples  | 7        |

Figure 7. Chromatographs showing retention time of 1 μl of butane with split ratio of 150:1.

the high density surface machined area and also the limited surface area available for bonding. Table II summarizes the shear test results for the seven samples.

After validating the bonding strength of the column, the bonding quality was further examined by gas chromatography technique. Testing was performed by attaching the inlet of the GC column to HP 6890 GC-FID system and changing the pressure over a wide operating range. For this experiment, the column temperature was kept at 30°C isothermally, inlet temperature set at 250°C with 1:150 split ratio. Helium was used as the carrier gas, and 1 μL of butane solution was injected for each pressure sets. Figure 7 shows the chromatographs of butane at four different pressure levels. As shown in the figure, the peak shape and the total area under the curve were remained constant for each inlet pressures; hence, no voids and crevices were observed.

Furthermore, the performance of the GC column was monitored to explore the separation capabilities of the column for a mixture of twenty one components listed in Table III. The column was connected to HP 6890 Fast-FID and the chromatograms of the 21 compounds were obtained by injecting 0.2 μl of the sample (split ratio of 400:1, Pressure 7.5 psi, and temperature 80°C and ramp rate 10°C/min). Figure 8 shows the chromatograms achieved using the 3 meter MEMS column.

Conclusions

This work demonstrates a new gold eutectic-fusion bonding for micro-fabrication of all silicon 3-meter gas chromatography column with a small footprint. The high temperature annealing technique was critical in improving the silicon bond quality, and the shear force measurement confirmed an effective permanent bond was formed. The bonding quality measurement using a mechanical force-displacement test can be used for quality control of the bonded columns. Characterization of the interface using SEM and EDX imaging indicated that the gold had diffused into the silicon surface, with little if any remaining at the interface. Evaluation of the columns by measuring the retention time for butane, at different inlet pressure levels showed a clearly resolved peak with decreasing retention time at higher pressure. The utility of silicon 3-meter column was demonstrated by separating a mixture of twenty one compounds with different Kovats retention index and molecular weights. Future work will address improving the temperature control of the column to enable higher temperatures to be reached during the temperature ramping, and demonstrating separations of other mixtures relevant to environmental sensing and food safety.

Acknowledgments

The authors thank the staff of Nanotechnology Research Center and the Agricultural Technology Research Program at Georgia Tech Research Institute for financial support.

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