A micro gas chromatography chip with an embedded non-cascaded thermal conductivity detector

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Abstract

We present the design, fabrication, and testing results of a single chip (2cm x 4cm) micro gas separation column (μGC) with an embedded non-cascaded micro thermal conductivity detector (μTCD). Our unique design coupled with RIE-Lag enabled 3D etching technology offers several advantages over previously reported designs including simple 2-mask fabrication and operation (no flow restrictors needed), capability for different flow velocities for the column and detector, low dead volume, low pressure drop, low detector power consumption, and an injection-event indicator. Our particular design is distinctly different from others in the number of fluidic ports (only 2 ports), channel design (circular cross section), and column type (open tubular). This μGC-μTCD chip separated and detected a 200nl sample mixture consisting of alkanes in less than 2 minutes with power dissipation less than 400mW.

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1. Introduction

Gas chromatography (GC) has proved to be the front-runner among the various analytical techniques used for chemical analysis of complex gas mixtures. It has widespread applications in medical diagnosis, environmental monitoring and petrochemical industries among others [1-3]. Micro Gas chromatography (μGC) is the art of miniaturizing the various components of the GC system to the point wherein a handheld, portable system can be realized. Such light-weight, low-power systems can facilitate quick, economical, and practically feasible analysis. In this paper, we present a monolithic integration of a separation column and a thermal conductivity detector (TCD) in a unique integration style. This offers multiple advantages over hybrid and alternative monolithic integration approaches [4-5]. Herein, we provide the 2-mask fabrication, testing and isothermal separation results of a 4-component mixture.

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2. Concept

The separation column, the most important component, is a long narrow channel whose walls are coated with a polymeric material known as a stationary phase. As the sample travels through the channel, the different components in the mixture interact with the stationary phase to different extent and consequently get separated [6]. The separated gases are detected at the end of the channel by a detector as they elute. Thermal conductivity detectors (TCDs) consist of a heater exposed to a carrier gas. Under normal operating conditions, the high thermal conductivity coefficient of the carrier gas sinks heat from the heater maintaining a particular temperature. However, a component with a lower thermal conductivity coefficient will sink heat to a lesser extent. This causes the temperature of the heater to increase which can in turn be mapped to its resistance. It is customary to introduce differential measurement against a heater that is not in contact with the sample due to ambient fluctuation.

The most novel and unique feature in this design is the absence of a reference channel. This was achieved by placing the reference heater close to the inlet as shown in Fig 1. While the components in the injected sample separate and pass under the detector close to the outlet, the reference heater is in contact with only the carrier gas. Thus, this method possesses the best intrinsic resistance to output drift with flow rate and does not require flow restrictors when compared to previous designs [5, 7-9]. Fluidic interconnects are unreliable and prone to failure in MEMS packaging. This design reduces the number of fluidic interconnects down to two.

3. Fabrication

The device was fabricated as an anodically bonded Pyrex-on-silicon stack as summarized in Fig 2(i). First, photoresist was spun on Pyrex and patterned. The metal heaters for the thermal conductivity detector were realized as a 200Å/600Å/150Å Ti/Pt/Au stack deposited by evaporation and patterned by liftoff. From Fig. 1, it can be observed that each heater can be broken into three sections, namely resistor, interconnect and bond pad. Each requires a different etch depth from the silicon side. The resistor portion is aligned to the separation channel. A shallow silicon etch is needed for interconnects to prevent contacts with silicon and minimize dead volume. To expose the bond pads, deep etching is required to facilitate the removal of silicon.

The requirement of obtaining multiple etch depths in a single silicon etch step was met by the use of a reactive ion etch (RIE) lag enhanced isotropic etch that was developed by our group [10-11]. Silicon was thermally oxidized to obtain a ~5000Å thick oxide layer. Together with photoresist, this layer serves as a bi-layer mask. Using different sized holes spaced apart at a specific distance, different predictable localized etch rates – and consequently, multiple etch depths - were obtained as shown in Fig 2(ii).
The silicon wafer with channels etched and the Pyrex wafer with the metal deposited on it, were aligned and bonded at a temperature of 300°C in air using a probe station modified to function as an anodic bonder. This was followed by two dicing steps. The Si/Pyrex thru-cut in Step (c) of Fig 2(i) recovered the individual chips while the Si cut itself exposed the bond pads. The shallow etch regions below interconnects were filled with epoxy and holes drilled through Pyrex for the fluidic ports. The resulting chip, with capillary tubes connected, is shown in Fig 3.

![Image](image1.png)

**Fig 2:** (i) summarizes the fabrication process flow (ii) gives cross-sectional views of the fabricated device showing the variation in etch depths obtained using the RIE-Lag enabled isotropic etch model.

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![Image](image2.png)

**Fig 3:** Packaged chip showing capillary tubes connected on both ends. The thermal conductivity detector is also visible, with resistors close to inlet and outlet.

### 4. Results and conclusion

The fabricated µGC chip with a 50cm-long, 140μm-wide, 70μm-deep separation column was coated with polydimethylsiloxane as the stationary phase using static coating method. A 10mg/ml concentration solution was used for coating. The µGC chip was evaluated in HP5890 GC system equipped with a flame ionization detector (FID). The FID was used in tandem with TCD for verification. Helium was used as the carrier gas at 5psi. The inlet and the detectors were maintained at 280°C. The reference and sample resistors of the on-chip TCD were connected in series with a current source and the resistor temperature was maintained around 83°C with power dissipation less than 400mW. It should be noted that the presence of the detector heaters elevated the temperature of the chip. A LabVIEW program was used to calculate the difference in the voltage of the two resistors and to record the results. Separation of a 200ml 4-component mixture (n-hexane, n-heptane, n-octane and n-nonane) in less than 2 minutes as detected by the embedded µTCD and the FID are shown in Fig 4. The initial negative spike in the response of the µTCD corresponds to the sample crossing the reference resistor at the inlet while the outlet resistance measures only the baseline.

![Image](image3.png)
We have demonstrated a monolithic integration of separation column and TCD. Our approach of placing the reference resistor close to the inlet provides for simpler pneumatic controls and robustness in mechanical handling. This development provides a lower cost, higher portability, and improved performance MEMS-based GC systems.

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