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A Micro Gas Chromatography System for VOCs Gas Mixtures Analysis

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Abstract

In this paper, we introduced a micro gas chromatography (GC) system, which integrated a micro GC column and a micro thermal conductivity detector (μTCD). The micro GC column with a high aspect ratio channel was integrated some micro-heaters which were placed on the surface and back of the micro GC column. These micro heaters can quickly enhance the temperature of the micro GC column with a ratio of 40℃/min, and the temperature can reach 140℃ in 4 minutes, therefore, the integrated micro GC column can greatly improve the separation speed and performance. The μTCD with four-filament thermal conductivity cell was proposed, and the dead volume of the thermal conductivity detector was almost zero because of the thermal conductivity cell and flow channel with a streamlined structure. From the separation experiment, the micro-GC system can rapidly detect the benzene, toluene and styrene with a sample concentration of 500 ppm, and the detection limit of the chromatographic system can be close to a few ppm. This micro-detection system can be widely used in environmental monitoring, food safety, fault diagnosis of transformer and other applications.

Keywords: Micro Gas Chromatography Column; Micro Thermal Conductivity Detector; Micro Gas Chromatography System

1. Introduction

Micro gas chromatography (μGC) systems[1,2] have the potential of being more portable, more robust, much cheaper and so on, compared with traditional GC system. The compactness and portability of micro GCs make them extremely suitable for health service, homeland security, industry pollution monitoring, and environmental analysis. The goal of this work is to develop a micro GC system which can be widely used in VOCs analysis, environmental pollution, and other fields.

2. The scheme of the micro GC system

In this paper, the micro-GC system is made up of a micro pump, a micro H_2 generator, two micro-needle valves, a micro GC column and a micro thermal conductivity detector. The sample was injected by the micro pump, and the flow velocity was regulated using the micro-needle valves. The micro GC column with a high aspect ratio channel was integrated four micro-heaters which can rapidly enhance the temperature, so the micro GC column can rapidly separate the mixture gas and obtain a very good separation performance. The micro thermal conductivity detector [3] with a four-filament thermal conductivity cell is proposed, The dead volume of the thermal conductivity cell was extremely small because of its streamlined structure, and the supported beam with high-strength, which was almost less susceptible to the impact of airflow, was formed by a diffusion of silicon layer, a silicon oxidation layer, and a silicon nitride layer. So the detection response, reliability and life of the thermal conductivity detector were greatly improved.

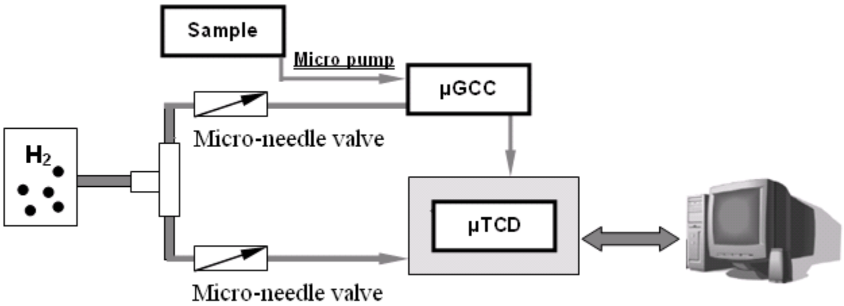

Fig.1. The scheme of the micro GC system.

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3. Fabrication

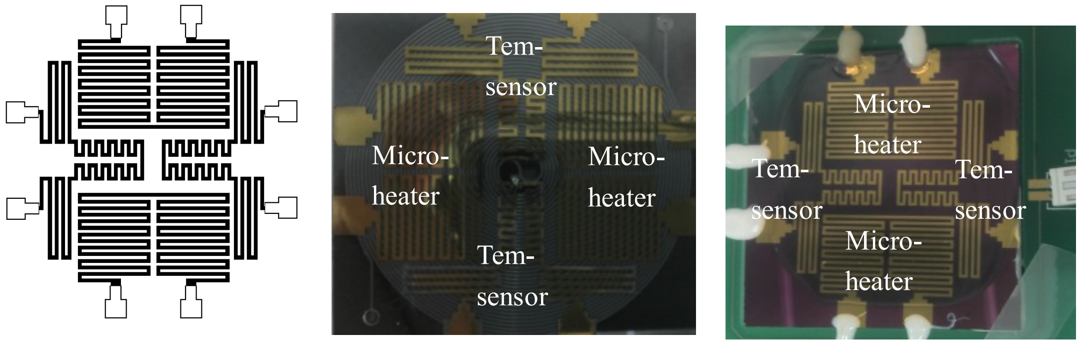
3.1 The fabrication of the integrated micro GC column

In order to reduce the volume of the micro-chromatography system, a micro-GC column, which was integrated some micro-heaters for rapidly heating the column, was designed in this paper. The advantage of this design was to eliminate the temperature control box in the micro chromatographic system. In addition, a high aspect ratio micro-channel was designed in order to improve the separation performance of the micro-column.

The process was as follows: Firstly, a 4000 Å low pressure chemical vapor deposition (LPCVD) silicon nitride film was deposited on the top of the silicon layer which served as the etch mask in following steps. Secondly, a thickness of approximately 2 μm photoresist was coated on the wafer and patterned as an etch mask for silicon nitride film. Subsequently, silicon nitride film without the protection of photoresist was etched by the reactive-ion etching (RIE) technology and the silicon surface was exposed. Then, a deep reactive-ion etching (DRIE) process was utilized to form the rectangular micro channels. The width and depth of the micro channels were 100 and 200 micros, respectively. Then the micro channels was emerged in 30% KOH buffer at 80□ and etched for ninety minutes until the depth of the channel was over 300 micros.

The micro heaters and the temperature sensor (the design is shown as Fig.2. (a)) were fabricated on the surface and back of the micro GC column. These micro heaters and micro temperature sensor were realized as a 200Å/1500Å Cr/Pt stack deposited by magnetron sputtering and patterned by liftoff. Then the glass cover plate was anodically bonded to the silicon wafer.

Finally, the GC column was coated with dimethyl polysiloxane (OV-1) as the stationary phase via a dynamic coating procedure.

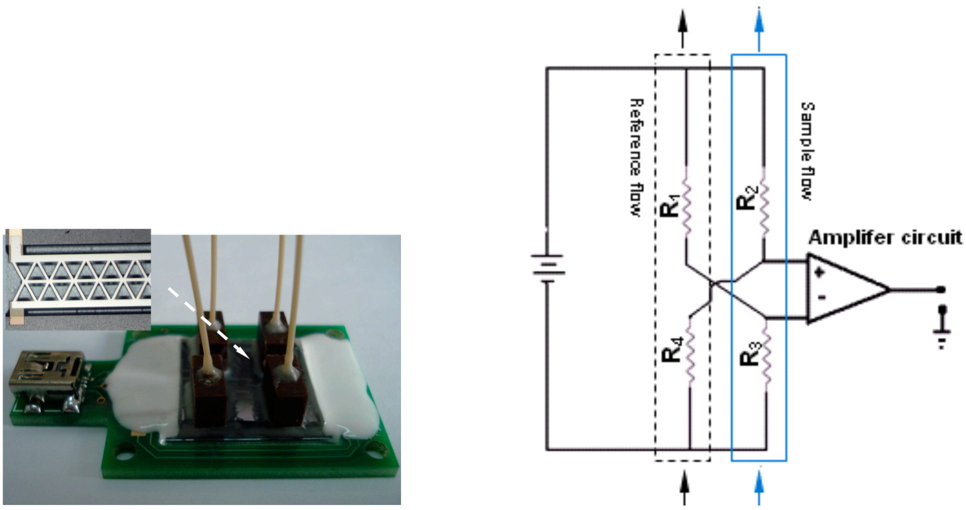


(a) (b) (c)

Fig.2. (a) The structure of the Micro heaters and micro temperature sensor,(b) the surface and (c) the back of the integrated GC column.

3.2 The fabrication of the μTCD

Because the detection response of the four-filament thermal conductivity cell was 2 times more than that of the two-filament one, the μTCD with four-filament thermal conductivity cell was proposed in this paper. What's more, the



(a) (b)

Fig.3. (a) The picture of the μTCD, (b) The scheme of a bridge circuit for μTCD detection

width and depth of the thermal conductivity cell and the flow channel were all the same size, and the airflow channel was a streamlined structure，so the dead volume of the thermal conductivity detector was almost zero. In addition, the filaments were supported by a three-layer structure beam formed by a diffusion of silicon layer, a silicon oxidation layer, and a silicon nitride layer in order to improve the reliability and life of the thermal conductivity detector.

The fabrication process of thermistors was shown as follows. A 15-μm thick layer of boron ions (B^+) was implanted into the surface of silicon as a mask for the corrosion of silicon and a supported beam for the thermistor. The concentration of B^+ was 1×10^{19} cm^{-3} which was high enough for the self-stop corrosion. A 5000 Å thick thermal silicon oxide film and a 4000 Å low pressure chemical vapor deposition (LPCVD) silicon nitride film were successively deposited on the top of the diffusion of silicon layer. The thermistors of the μTCD were realized as a 200Å/1500Å Cr/Pt stack deposited by the magnetron sputtering technology and patterned by the lift-off technology, and the resistances of the thermistors were designed for 100 ohms in order to improve the detection response of the bridge. Then the same channel was etched on the glass wafer using HF buffer, and the glass cover plate was anodically bonded to the silicon wafer (The picture of the μTCD is shown as Fig.3).

4. Results and conclusion

4.1 The temperature response of the integrated micro GC column

These heaters cover the whole of micro GC column which can evenly heat all the parts of the GC column and improve the chromatogram peak. The resistance of the each heater was 8 Ω, and the applied voltage on these heaters was 9V, Fig.4 was the temperature response characteristics curve of the integrated micro GC column. The variation of the temperature was almost linear relationship till 200 s and the

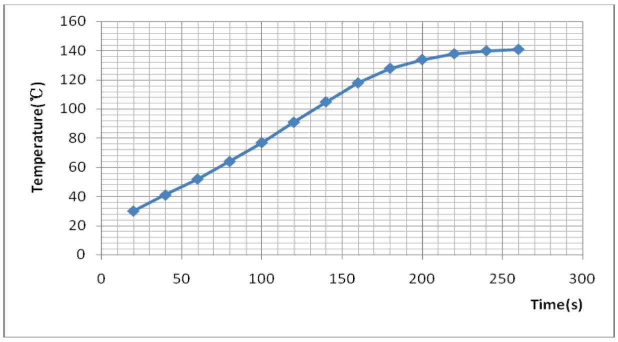


Fig.4 The temperature response of the integrated micro GC column

increase of the speed was close to 40□ in every minute. Then, the temperature change was slower, and tends to balance. So the micro integrated GC column had very strong self-heated performance, which can greatly improve the GC column separation speed and separation properties.

4.2 Rapid detection of VOCs gas mixtures

Experiment was carried on our self-developed micro-GC system. The pure H_2, which was obtained by a micro-H_2 generator, was acted as the carrier gas and the flow rate was regulated at 2 ml/min. The sample was the mixtures of benzene, toluene and styrene. The concentration of each sample was 500ppm. The sample was injected at time zero using the micro pump.

The separation curve of benzene, toluene and styrene was shown in Fig.5. The response time of benzene was less than 40S. Moreover, the three samples were perfectly separated in 3 min, and the chromatogram didn't show obviously peak tailing. Resolution,which is called overall separation efficiency, can be defined as the difference of retention value between two

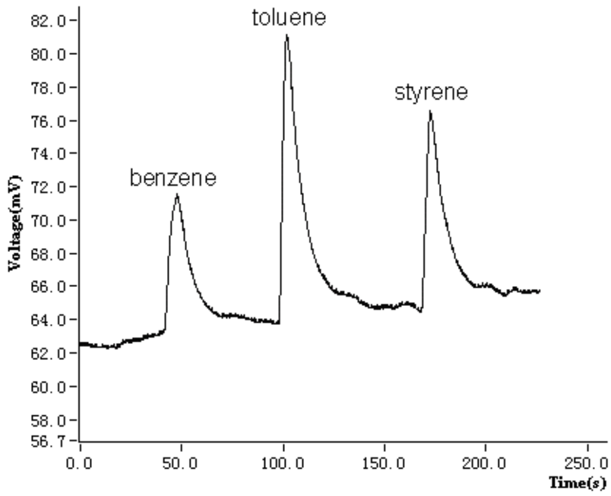


Fig.5 is the separation curve of benzene, toluene and styrene using the micro GC system, and the flow velocity is 2 ml/min.

adjacent chromatography peaks divided by the half of the sum of these two peak's bottom width, so the resolution can be described by equ (1)

$$R = \frac{t_{r_2} - t_{r_1}}{\frac{1}{2}(w_1 + w_2)} = \frac{2(t_{r_2} - t_{r_1})}{w_1 + w_2} \quad (1)$$

Where t_r is the retention time, and w is the width of the chromatography peak's bottom width.From the resolution equation (1), the resolution of benzene and toluene was computed as 1.5, the resolution of toluene and styrene is over 2.3, and the separation of the gas mixture was very ideal.

Seen from the chromatographic curve, The amplitude of benzene chromatographic peak was over 10mV, The amplitude of toluene chromatographic peak was over 20mV, and the amplitude of styrene chromatographic peak was over 15mV, the detection limit of the chromatographic system was close to a few ppm according to the relationship between the peak area or peak height and the sample concentration. The micro-chromatography system can be widely used in environmental monitoring, food safety, fault diagnosis of transformer and other applications.

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References

[1] Y.E. Wu, K. Chen, C.W. Chen, K.H. Hsu, Fabrication and characterization of thermal conductivity detectors (TCDs) of different flow channel and heater designs, Sensors and Actuators A, 100 37-45(2002).

[2] D. Cruz, J.P. Chang, S.K. Showalter, et al., Microfabricated thermal conductivity detector for the micro chemLab, Sensors and Actuators B, 121,414-422(2007).

[3] J. Sun, et al., Design, modeling, microfabrication and characterization of novel micro thermal conductivity detector. Sens. Actuators B: Chem,160（1）936-941(2011).