THE EXPLORATION OF MESOPOROUS SILICA AS A STATIONARY PHASE SUPPORT FOR SEMI-PACKED MICRO-FABRICATED GAS CHROMATOGRAPHIC (GC) COLUMNS

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ABSTRACT

This paper reports the use of mesoporous silica as a stationary phase support for serpentine semi-packed micro-fabricated gas chromatographic (GC) columns. Herein, polydimethylsiloxane (OV-101) is used as the stationary phase. It is demonstrated that gaseous alkane C1-C4 can be well separated by using the micro-fabricated GC columns in 2 m, rather than the 25-30 m of conventional capillary columns. Besides, the chromatographic resolution of mesoporous silica column for C1-C2 is 120% higher than that of the same GC column without mesoporous silica, which can be contributed by the greatly increased overall surface area of the mesoporous silica column.

INTRODUCTION

Gas chromatography (GC) is one of the most widely applied methods of identification in analytical chemistry [1]. It is a technology for the separation and analysis of complicated gas mixtures, has been widely used in industry, agriculture, construction and scientific research. The conventional gas chromatography system has the powerful separation ability of gas mixtures. Meanwhile, it has the disadvantages of large volume, heavy weight, long separation time and high energy consumption due to the use of a big oven. In this situation, the miniaturization of gas chromatography system is an urgent problem to be solved.

Micro-electro-mechanical system (MEMS) technology is considered to be the most effective way to produce a micro gas chromatography (GC) system [2]. The separation column is an important component of the GC system. The first efforts to develop a micro GC column began in the late 1979s at Stanford University, the column was rectangular spiral format [3]. Since then, great progress on research for micro GC columns has been obtained. Micro GC columns has been designed in spiral [4], serpentine [5], multicapillary [6], open [7] and semi-packed format [8]. For example, R. R. Reston in Texas Christian University made the spiral format GC column with a length of 0.9 m, a cross-section width of 300 μm and a depth of only 10 μm. It was fabricated by wet etching to separate and detect NH_3 and NO_2 [9]. Howerver, it has been proved that utilizing of serpentine column holds better separation efficiency than spiral format [10].

Compared to open micro GC columns, the semi-packed GC columns have the large surface area. The semi-packed column with embedded square posts was firstly developed by Agah's group [8]. Recently, more and more researches have focused on the semi-packed column. For example, in the work of Sun et al, the group fabricated a semi-packed micro column with embedded circular micro-posts. The semi-packed column has the better separation efficiency because of the micro-posts array developed for increasing the overall surface area of the columns which is able to support more of the stationary phase [11].

In addition, stationary phase plays a very important role in the separation capability of GC columns [12]. OV-101 is frequently used as a stationary phase of GC columns [13]. As is known, the surface area of the stationary phase is a key factor in determining the separation capability of GC columns. This paper will show a complete set of manufacturing and testing of a semi-packed serpentine micro fabricated GC column with mesoporous silica as the stationary phase support. The main difference between the previous work and the one reported here is that we use mesoporous silica, which has a high overall surface area, as the GC stationary phase support to improve the separation resolution of columns.

EXPERIMENTAL SECTION

Microchannels fabrication

From the early wet etching technique to the later deep reactive ion etching (DRIE), the micro GC column has been developed for more than 30 years. Wet etching technique was used in the manufacture of micro column in the early period. For example, in the 1995s, the E.S. Kolsear and et al at Texas Christian University in the United States designed the spiral micro GC column with a length of 0.9 m, a depth of 10 μm, and a width of 300 μm [14]. In the late 1990s, DRIE technique as the representative of the new MEMS silicon processing technology has been rapidly developed, leading to the production of micro-column with fast etching rate and high etching depth. Moreover, the high aspect ratio columns etched by DRIE technique would have better separation efficiency. Thus, we will utilize DRIE technique to etch micro GC columns.

The fabrication is performed on a 4 inch, 530 μm thick double-side polished silicon and is accomplished using one mask. The silicon wafer processing starts with growing a thick layer of SiO_2 that is served as a mask for silicon etching. AZ4620 photoresist is spin-coated at 1500 rpm to achieve ~9 μm thick photoresist layer. The wafer is then patterned using mask aligner and is hard-baked for 3 min at 105˚C. Afterwards, anisotropic etching of silicon is performed using DRIE which results in the creation of 250 μm-wide and 304 μm-deep channels with 40 μm in diameter embedded circular

micropillars, as shown in Figure 1a. Then the photoresist is stripped off.

Integration of mesoporous silica in the micro column

The mesoporous silica is prepared using sol-gel method: including hydrolysis of precursor, self-assembly with surfactant, dip-coating and removal of surfactant [15]. Firstly, the mixed solution of 50 ml ethanol, 50 ml TEOS, 4.14 ml deionized water and 1 µl 36.5 wt% HCl are heated to 60 °C. Secondly, 16.6 ml deionized water and 76 µl 36.5 wt% HCl are added into the solution. After stirring at room temperature for 15 min, the solution is maintained at 50 °C for 15 min and then diluted with 250 mL of ethanol. Then, 8.4 g CTAB is added. Finally, the solution is stirred for 1h at room temperature. The thin mesoporous silica film is deposited onto the inner surface of the fabricated micro column by dip-coating process. Herein, dip-coating is carried out at the rate of 61.8 mm/min. After removal of the solvent by storing the micro GC column in the dryer for 72 h, the calcination is carried out in 550 °C to remove the surfactant, which results in the final pore structure.

Consequently, the final mesoporous structure on the inner surface of the micro channels is shown in Figure 1b.

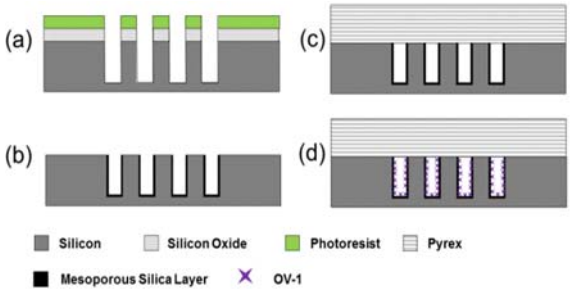

Figure 1: The fabrication process of the serpentine semi-packed gas chromatographic columns (GC) which use mesoporous silica as the stationary phase support and coated with the polydimethylsiloxane (OV-101): (a) deep reactive ion etching (DRIE); (b) mesoporous silica coating; (c) Silicon-glass bonding; (d) coated with OV-101.

Silicon-glass bonding and Dicing

The silicon wafer is anodically bonded to a glass wafer, which is shown in Figure 1c. Anodic bonding is carried out at 350 ˚C and 1200 V for 45 min. After bonding, the wafer is cut using dicing technology, at the same time cleaned by DI water, which is shown in Figure 1c.

The static coating of OV-101

There are two coating methods of the stationary phase: dynamic coating [16] and static coating method [17]. With dynamic coating, the coating solution is pushed at a constant flow rate by applying pressure through the inert gas, leaving a film of stationary liquid on the inner wall of the column. After the coating is completed, the excess solvent is evaporated by a continuous stream of gas. Static coating method is widely used for stationary phase coating. For static coating, the entire column is filled with the coating solution, then the column is sealed at one end and vacuumed at the other end, and slowly evaporate the solvent. In general, static coating is better than dynamic coating. First of all, through static coating almost all of the stationary phase is deposited onto the column wall; and secondly, since the flow of the stationary phase during deposition is reduced, the deposited stationary film is more homogeneous, which will obtain a better peak shape.

In our experiment, the stationary phase is deposited on the mesoporous silica layer by static coating (Figure 1d). The stationary phase was OV-101 that is dissolved in n-pentane solution with a volume ratio of 4%. The entire column is filled with the coating solution, then the column is sealed at one end and vacuumed at the other end in the vacuum chamber.

EXPERIMENTAL RESULTS

The SEM images of the micro-fabricated column with serpentine semi-packed configuration are presented in Figure 2. The width of a channel, the diameter of micro-post, the distance between adjacent micro-posts and the distance between micro-post and wall are 250 µm, 40 µm, 30 µm and 35 µm, respectively.

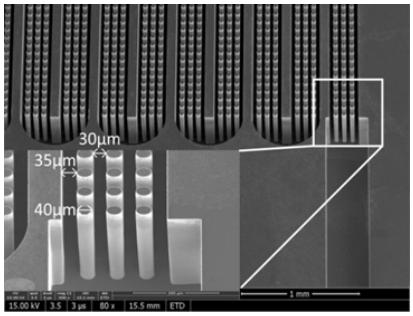

Figure 2: The SEM images of the serpentine semi-packed micro fabricated GC column.

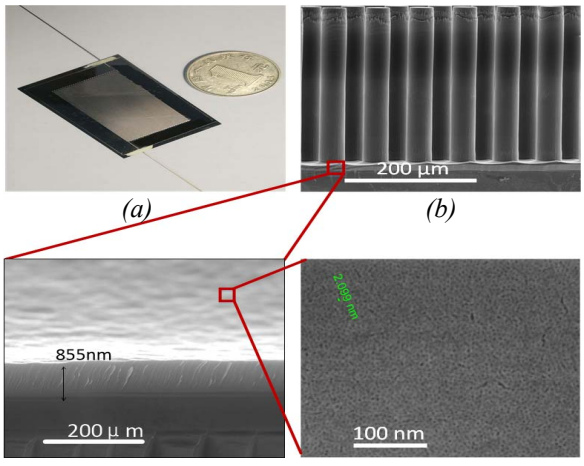

Figure3 :(a) Packaged chips of the micro GC column; (b) The cross section of micro GC column ; (c) The thickness of mesoporous silica is 855nm; (d) The pore size of mesoporous silica is approximately 2 nm.

Table 1. Separation results between the micro GC column with and without mesoporous silica support

Analytes	Separation results (with same carrier gas flow rate of 2.2mL/min)			
	Without Mesoporous silica		With mesoporous silica	
	Retention time (min)	Resolution	Retention time (min)	Resolution
C1	0.66	0	1.23	0
C2	0.69	0.46	1.43	1.01
C3	0.77	0.84	1.96	1.04
C4	1.10	1.34	3.67	1.23

The photograph of the fabricated GC column chip is shown in Fig 3a, and its size is 47 mm × 31 mm. The cross section of GC column is shown in Figure 3b. Figure 3c and 3d show that the thickness and the pore diameter of mesoporous silica are 855 nm and 2 nm, respectively.

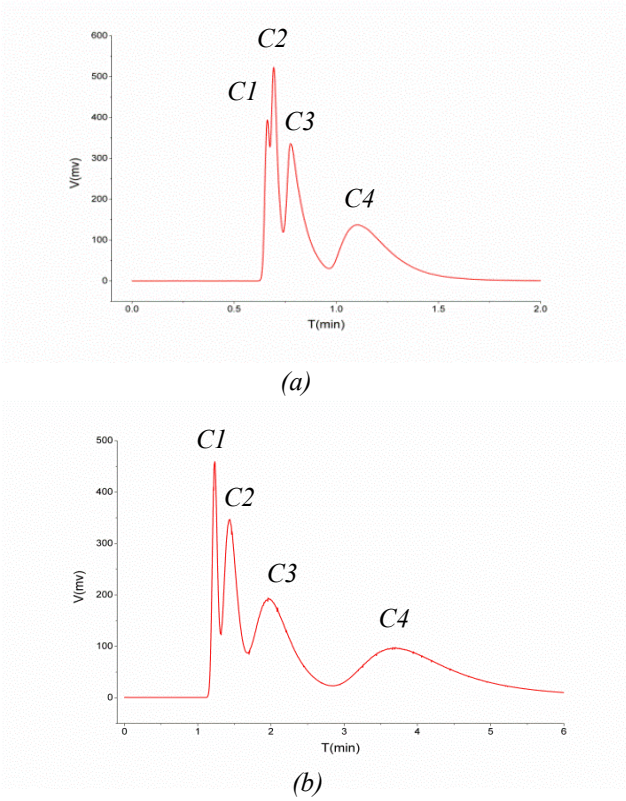

Figure 4: The separation effect of the micro GC column without (a) and with (b) mesoporous silica support

In order to evaluate the separation capability of our micro-fabricated GC column, separation experiment on the mixture of gaseous alkane (C1-C4) is performed on a commercial GC setup. As shown in Figure 4, we can basically separate the mixture of gaseous alkane (C1-C4) with same carrier gas flow rate of 2.2mL/min. Compared with Figure 4a (without mesoporous silica support) , Figure 4b shows that the C1-C2 can get a very good resolution in the micro GC columns with mesoporous silica support. As shown in Table 1, the retention times of C1-C4 in the column without mesoporous silica support are 0.66, 0.69, 0.77, 1.10, respectively. And at the same time the resolutions of C1-C2, C2-C3, C3-C4 are 0.46, 0.84 and 1.34. In the GC columns with mesoporous silica support, the retention times of C1-C4 are as follows: 1.23, 1.43, 1.96, 3.67. Meanwhile, the resolutions of C1-C2, C2-C3, C3-C4 are 1.01, 1.04, 1.23, respectively.

The results show that the retention time of the column with mesoporous silica is twice longer than that of the column without mesoporous silica, which indicates that the mesoporous silica columns have better separation capability for gaseous alkanes. Besides, the resolution of C1-C2 in the micro GC column with mesoporous silica support has been increased by 120% to 1.01 compared to the column without mesoporous silica support. The main reason is that the column with mesoporous silica support has more overall surface area than the column without mesoporous because of mesoporous silica with large specific surface area.

CONCLUSION

In this work, the semi-packed micro GC columns with mesoporous silica as a stationary support have been successfully fabricated by using MEMS technique. Testing results show that the chromatographic resolution of the micro GC column with mesoporous silica for C1-C2 is 120 % higher than that of the same GC column without mesoporous silica, which demonstrates the potential of mesoporous silica film as a stationary phase support for micro GC columns. In summary, we not only put forward a new method to increase the overall surface area of GC column, which is simple, low

cost wet chemistry method, but also use the 2-m-long column to achieve a good separation resolution of nonpolar n-alkanes (C1-C4).

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