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Improved separation of micro gas chromatographic column using mesoporous silica as a stationary phase support

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ABSTRACT

In this paper, a novel and facile way to improve the separation of micro gas chromatographic column is presented which utilizes the mesoporous silica thin film as the stationary phase support. A serpentine semi-packed column is fabricated based on a micro-electro-mechanical system (MEMS) technology and polydimethylsiloxane is used as the stationary phase. The chromatographic resolution of C6-C7 increases from unseparated to 7.44 after depositing mesoporous silica thin film as the stationary phase support in the separation of a mixture of heavy hydrocarbons (C6-C10), and the separation efficiency is as high as 9290 plates/m. Meanwhile, in the separation of a mixture of benzene series (gas mixtures of benzene, toluene and paraxylene), the chromatographic resolution of benzene and toluene can also be increased by 483%. Those outstanding results indicate that using the mesoporous silica as the stationary phase support is an effective way to improve the separation efficiency of the gas chromatographic column.

1. Introduction

Gas chromatography (GC), a technology for the separation and analysis of complicated gas mixture, has a wide range of applications in the fields of analytical chemistry, such as pharmaceutical, oil exploration, environmental monitoring and material purification [1–7]. Generally, a complete GC system is composed of an injector, a GC oven containing column and a detector [8,9]. The conventional GC system normally has disadvantages of large volume, heavy weight and long separation time, which restrict its applications in on-site and real-time monitoring [10]. Hence, the miniaturization of GC system is an urgent problem to be solved [11–13], and the realization of micro GC column is the key factor [14–16].

Micro-electro-mechanical system (MEMS) technology is an effective way to realize the micro GC column [17–19]. In the early time, the research of micro GC (μGC) column was focused on the structural design. The shape of microchannel cross-section generally was circular or semi-circular, which was manufactured by a wet etching technique. With the development of MEMS technology, deep reactive ion etching (DRIE) technique has been used to design and fabricate μGC columns, whose cross-section generally is high-aspect-ratio rectangular shape, which could improve separation efficiency through making the gas molecules reach balance state rapidly between the stationary phase and mobile phase. Recently, the internal structure of micro channels has been in-depth researched. And the μGC columns usually can be classified into three types: open, semi-packed and packed μGC columns. The semi-packed μGC columns, which are usually considered to be a superior choice, can enhance the separation efficiency through providing a larger area of the stationary phase to adsorb more gas components compared with the open μGC columns, and produce a lower pressure drops compared with the packed μGC columns [20]. Square and circular micro-posts semi-packed μGC columns have already been researched [21–23]. However, due to the restriction of the MEMS technology, the further increase of the surface area is hard to achieve.

Stationary phase supports, which usually are the nanostructure materials possessing high specific surface area deposited on the inner surface of the μGC columns, could efficiently increase the surface area of the stationary phase [24]. Gold nanoparticles [25], silica nanoparticles [26], and alumina [27] have already been developed as the novel stationary phase support to improve the separation performance lately. Mesoporous materials with a pore size of 2–50 nm possess a large specific surface area and ordered structure. In particular, owing to easy preparation, low cost, fine chemical stability and mechanical stability, mesoporous silica (MS) has attracted considerable attention in a variety of fields such as separation, catalysis, drug delivery, sensors, photonics, and environmental remediation [28–30]. However, there are few

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reports about MS served as the stationary phase supports for the μGC columns.

In this paper, mesoporous silica synthesized using a sol-gel method, is deposited onto the inner surface of the μGC columns in a dip-coating process as the stationary phase support. The serpentine semi-packed μGC column with high aspect ratio is fabricated based on MEMS technology and polydimethylsiloxane is used as the stationary phase. The μGC columns with and without mesoporous silica support are utilized to test the separation of a mixture of nonpolar n-alkanes (C6-C10) and benzene series (gas mixtures of benzene, toluene and paraxylene).

2. Experimental section

2.1. Materials

Tetraethylorthosilicate (TEOS), 36.5 wt% HCl, toluene and ethanol were purchased from Shanghai Chemical Corporation. Hexadecyltrimethyl ammonium bromide (CTAB) was purchased from Sigma-Aldrich (St. Louis, Mo, USA). Polydimethylsiloxane (PDMS) (OV-101) was purchased from Aladdin (L.A.,USA). Heavy hydrocarbons (C6-C10) were purchased from Aladdin (L.A.,USA) and benzene series (gas mixture of benzene, toluene and paraxylene) were purchased from Shanghai Bo Shi Chemical Co., Ltd.

2.2. Microchannels fabrication

The fabrication of the μGC columns is illustrated in Fig. 1. The fabrication was performed on a 4 in., 530 μm thick double-side polished silicon and accomplished using one mask. Typically, the silicon wafer processing started with growing a thick layer of SiO_2 served as a mask for silicon etching (Fig. 1a). AZ4620 photoresist was spin-coated at 1500 rpm to achieve ~9 μm thick photoresist layer. Then, the wafer was patterned using mask aligner (Fig. 1b) and hard-baked for 3 min at 105 °C. Subsequently, SiO_2 without photoresist protection was etched away by Samco RIE. Afterwards, anisotropic etching of silicon was performed using DRIE which results in the creation of 250 μm-wide and 304 μm-deep channels with 40 μm in diameter embedded circular micro pillars, as shown in Fig. 1c. After that, the photoresist was stripped off and the SiO_2 layer on the surface of the wafer was eliminated.

2.3. Integration of mesoporous silica in the μGC columns

The mesoporous silica was prepared using a sol-gel method: including hydrolysis of precursor, self-assembly with surfactant, dip-coating and removal of surfactant [31]. Firstly, the mixed solution of 50 ml ethanol, 50 ml TEOS, 4.14 ml deionized water and 1 μl 36.5 wt% HCl were heated to 60 °C. Secondly, 16.6 ml deionized water and 76 μl 36.5 wt% HCl were added into the solution. After stirring at room temperature for 15 min, the solution was maintained at 50 °C for 15 min and then diluted with 250 ml of ethanol. Then, 8.4 g CTAB was added. Finally, the solution was stirred for 1 h at room temperature. The thin mesoporous silica film was deposited onto the inner surface of the fabricated μGC columns by a dip-coating process at the rate of 61.8 mm/min. After removal of the solvent by storing the μGC columns in the dryer for 72 h, the calcination was carried out in 550 °C to remove the surfactant and produce the final pore structure. Consequently, the final mesoporous structure on the inner surface of the micro channels is shown in Fig. 1d.

2.4. Silicon-glass bonding and dicing

The silicon wafer was anodically bonded to a glass wafer at 350 °C and 1200 V for 45 min, (Fig. 1e). After bonding, the wafer was cut using dicing technology and cleaned by DI water at the same time.

2.5. The static coating of PDMS

In order to form a thin stationary phase film, the fabricated μGC columns were coated via a static coating procedure. For static coating, the entire μGC column was filled with the coating solution, and then the μGC column was sealed at one end and vacuumed at the other, and slowly evaporated the solvent. In our experiment, the stationary phase was dissolved in n-pentane solution with a volume ratio of 1% by static coating (Fig. 1f).

2.6. Instruments and measurements

The scanning electron microscope (SEM) images through a field-emission scanning electron microscope (FESEM) were taken under an acceleration voltage of 2 kV. Transmission electron microscopy (TEM)

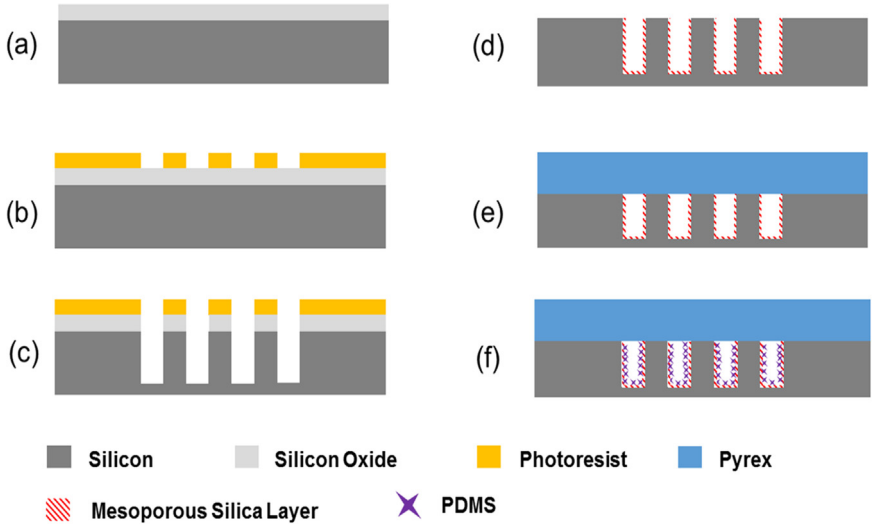

Fig. 1. The fabrication process of the serpentine semi-packed μGC columns: (a) silicon oxide deposition, (b) photolithography, (c) DRIE; (d) mesoporous silica coating; (e) silicon-glass bonding; (f) PDMS coating.