HIGHLY STABLE SURFACE FUNCTIONALIZATION OF HIGH-ASPECT-RATIO MICROGAS CHROMATOGRAPHY COLUMNS USING LAYER-BY-LAYER SELF-ASSEMBLY OF SiO_2 NANOPARTICLES

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ABSTRACT

A novel selective surface functionalization of 3D micro-silicon channels using a SiO_2 nanoparticles (NPs) coating deposited using Layer-by-Layer (LbL) self-assembly technique is reported here. Additionally, application of SiO_2 NPs coating as a stationary phase for chromatographic separation is also presented for the first time. Compared to previously reported techniques, this method enables a simple, low-cost and parallel processing scheme in obtaining homogenous and stable NPs coatings inside the microfluidic channel. Moreover, the reported scheme also provides good repeatability and ease of control over the coating thickness. The SiO_2 NPs functionalized microfabricated gas chromatography columns with wide single capillary channels (1 m-long, 150 μm -wide, 240 μm -deep) and very narrow multicapillary channels (25 cm-long, 30 μm -wide, 240 μm -deep, 16 parallel channels) successfully separated a multicomponent gas mixture with a wide range of boiling points.

INTRODUCTION

Microgas Chromatography (μGC)

Gas chromatography (GC) is a reliable chemical analysis technique that is used to separate and identify the constituents of complex gas mixtures. GC has applications in vast areas such as environment monitoring, food processing, pharmaceutical industry, biomedical science, forensic and trace analysis. A chromatographic process (schematically shown in Fig. 1) starts with the injection and vaporization of an unknown sample mixture (analytes); after which the analytes traverse through the separation column via a carrier gas (mobile phase). Columns are typically coated with a polymer (stationary phase) to physically separate the constituents of a mixture into separate compounds in a time domain. Afterwards, the separated components are eluted into a detector that generates a chromatogram based on the retention time of each compound. Each

peak in a given chromatogram represents a particular compound.

Traditional bench-top GC instruments, though widely used for over 50 years, are bulky, expensive, time and energy consuming. Due to recent advancement and emergence of microelectromechanical systems (MEMS), energy-efficient integrated μGC systems have attracted considerable attention because of its portability, fast analysis time, and low cost [1-3]. This system, upon complete realization, could enormously expand the range of GC applications in *in-situ* air quality monitoring, biomedical analysis, and homeland security. As a key component in a μGC system, conventional meters-long separation columns are replaced with coin-sized microfabricated silicon columns. The separation ability and efficiency of the column is directly related to the quality of the stationary phase. Using conventional coating techniques for rectangular-shaped microfabricated columns present major challenges towards getting reproducible and uniform coating. Conventional coating techniques also suffer from limitation in high temperature applications and poor stability (organic coatings) or requirements of expensive instruments and elaborate operation (inorganic coatings) [4-7]. The high thermal stability and high surface area of SiO_2 NPs present an excellent candidate for the stationary phase if employed using simple and low cost methods.

Layer-by-Layer (LbL) Self-Assembly Technique

Developed first in 1991[8], the LbL self-assembly technique was utilized to develop Ionic Self-Assembly Multilayers (ISAM), which have been widely used in electromechanical actuators [9] as well as in electro-optical and electrochromic devices [10, 11]. In short, by alternatively dipping the substrate into two aqueous solutions of materials with opposite charges (positive and negative), LbL thin films of the two materials, bonded together by electrostatic force, will build up on each other (two adjacent layers of those two materials are called one bilayer). Thorough rinsing in between each deposition step washes away excess coating materials from the previous stage while leaving enough surface charge for the material to be electrostatically deposited in the next step. Thus, uniform, dense, and sturdy stacks of layers can be deposited on the surface of the substrate with a wide variety of configurations. Additionally, a desired film thickness can be achieved by simply terminating the procedure at a certain number of bilayers. Therefore, with a relatively simple concepts and straightforward operations, the LbL self-assembly technique could be conveniently incorporated into the manufacturing of silicon-based μGC devices. In this article, by utilizing the LbL technique for the first time, high-aspect-ratio (HAR) μGC columns with different configurations are functionalized with SiO_2 NPs coatings used as a stationary phase.

FABRICATION

The fabrication scheme incorporating LbL self-assembled SiO_2 NPs coating, schematically shown in Fig. 2, can be divided into three major steps, which include column fabrication, LBL

Figure 1. Schematic of a GC system

deposition of NPs, and anodic bonding of the silicon substrate with Pyrex followed by deactivation of the silica surface.

Column Fabrication

The fabrication of HAR 1 m-long, 150 μm -wide, 240 μm -deep single capillary columns (μSCC) and 25 cm-long, 30 μm -wide, 240 μm -deep multicapillary columns (μMCC) with an array of 16 channels (Fig. 3H) working in parallel starts with anisotropic etching of plain silicon wafers. In the first step, wafers are spin coated with AZ9260 photoresist at 3000 rpm, soft-baked at 110°C for 1 minute and exposed for 45 seconds using a mask aligner (MA-6). After development using AZ400K, wafers are hard-baked at 110°C for 2 minutes. Deep reactive ion etching (DRIE) with photoresist as an etch mask is used to etch the wafers in order to get the desired channel dimensions. Afterwards, the wafer is diced into individual devices. Selective deposition of NPs inside the channels is achieved by using a liftoff procedure explained in the next section (Step 1, Fig. 2).

LbL Deposition of SiO_2 NPs

Keeping the photoresist intact, the LbL deposition of SiO_2 NPs inside HAR microfluidic channels starts with alternatively dipping each device into a positively charged long-chain inert polymeric aqueous solution (10 mM polyallylamine hydrochloride, PAH, from Sigma-Aldrich), and negatively charged SiO_2 NPs suspension (Nissan Chemical, 45 nm average particle size). Because of the much narrower channels, the μMCC column deposition uses the SiO_2 NPs suspension at 1/3 of its original concentration. This prevents the formation of bulky NPs structures between the channel walls. Following our earlier reported findings [11] to guarantee excellent PAH/ SiO_2 NPs LbL coating uniformity, the pH value of the PAH solution and SiO_2 NPs suspension are adjusted to the values of 7.0 (± 0.1) and 9.0 (± 0.1), respectively, by adding HCl and NaOH solutions. The LbL coating is then performed in an automatic dipping system (StratoSequence VI Robot, nanoStrata Inc.) in which every 2.5 minutes of PAH and SiO_2 NPs coating step is followed by three 1 minute DI water rinsing steps (Step 2, Fig. 2). The LbL deposition scheme presented here affords a homogenous SiO_2 NPs coverage both on the interior microchannel surfaces and on the photoresist at the top of chip. After coating, the samples are rinsed thoroughly with deionized (DI) water and dried with low flux nitrogen. NPs coated devices are then dipped in acetone and sonicated for 12 minutes. This liftoff procedure removes the NPs deposited on photoresist without removing the coating inside the trenches. The yield of lift-off process is important especially for the microfluidic applications in which the NPs coated silicon channels are to be sealed with a glass substrate (Step 3, Fig. 2).

Anodic Bonding and Deactivation of the Silica Surface

Before anodic bonding, the devices are first calcinated in a furnace at a high temperature (500°C) for 4 hours to fuse the SiO_2 NPs together and to ensure the stability of the coating during temperature programming of the GC columns. Afterwards, the silicon trenches are sealed to a Pyrex wafer using anodic bonding at 400°C and 1250 V (Step 4, Fig. 2). Next, deactivated capillary tubes (220 μm outer diameter, 100 μm internal diameter, 25 cm length) are installed at the inlet and outlet ports using epoxy. Then, 10 mM chlorodimethyl octadecyl silane (CDOS) diluted in toluene is

pumped into the chip by nitrogen (Step 5, Fig. 2). This overnight process deactivates NPs and the Pyrex cover surface [12]. Finally, the solvent is blown out by nitrogen and the device is ready for chromatographic analysis.

Figure 2. Schematic process flow of SiO_2 NPs coating using Layer-by-Layer self-assembly technique in the Si trench.

CHARACTERIZATION OF SiO_2 NPS COATING

As displayed in Fig. 3 (A-D), the bottom and sidewalls of the trenches are completely covered by SiO_2 NPs, while at the same time NPs are neatly removed by the lift-off process from the top surface. This is the first successful demonstration of combining microlithography and LbL self-assembly to selectively deposit NPs on the interior surfaces of silicon microchannels. Fig. 3E and Fig. 3F show the SEM images of 5 and 10 bilayers of SiO_2 NPs deposited inside silicon trenches, respectively. The thickness measured directly from the SEM images are 261 nm to 316 nm, 399 nm to 486 nm, and 554 nm to 667 nm for 5, 10, and 15 bilayers, respectively. Although a lower concentration of SiO_2 NPs suspension is used for μMCC , the 10 bilayers coating inside its channel (Fig. 2G) has approximately the same thickness (396 nm) as the 10 bilayers coating inside the μSCC (Fig. 2H). This means the coating for the SiO_2 NPs suspension at 1/3 of its original concentration is sufficient to deposit a layer of SiO_2 NPs over the previous PAH layer to neutralize and reverse the surface charge, while the excess SiO_2 NPs during the μSCC coating with higher concentration suspension is washed off during the rinsing steps.

Figure 3. SEM images of the 10 BLs SiO_2 NPs coated single capillary column (A-D), on the side wall (B), bottom of the channel (C-D); cross-section view of silicon trench with 5 BLs (E) and 10 BLs of SiO_2 NPs coating (F). Optical image of multicapillary column (G) and the SEM image of its cross-section with 10 BLs SiO_2 NPs coating on the side wall of Si trench (H).

SEPERATION TEST AND RESULTS

Experimental Setup

A commercial GC system (HP 5890 Series II), equipped with an autosampler, electronic pressure controller, and flame ionization detector (FID), was used for characterizing the separation ability of the μGC columns with the SiO_2 NPs stationary phase. Highly purified nitrogen (from Airgas Inc.) was used as carrier gas. Inlet and detector temperatures are set to 280°C and the split ratio is set to 100:1. Standard chemicals were purchased from Sigma-Aldrich and used for all experiments.

Separation Results

In order to evaluate the chromatographic performance, the functionalized μGC columns were placed in a GC oven. All columns were first purged with dry nitrogen to remove any trapped

Figure 4. Example of 9 alkane compounds separation by two 10 BLs SiO_2 NPs coated MEMS GC columns (A) and one column before and after 24 hours conditioning under 7.5 psi at 160°C (B).

Figure 5. Chromatographic separation result by a 10 BLs SiO_2 NPs coated MEMS GC multicapillary column for the 1st and 15th injection.

oxygen in the system. The columns were then conditioned gradually from ambient temperature to slightly above the maximum

operating temperature (120°C) at a temperature ramp rate of 1°C/min and a constant carrier gas flow of 7.5 psi until a constant baseline was observed.

The effectiveness of the SiO₂ NPs coating as a stationary phase for different channel geometries was tested on both μ SCCs and μ MCCs. All the chromatograms in Fig. 4 (μ SCC) and Fig. 5 (μ MCC) exhibited successful separations of alkanes (n-pentane, n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-pentadecane, n-hexadecane and n-heptadecane) spanning a wide range of boiling points (32°C ~202°C) with high stability and repeatability (less than 4% deviation in retention time). Fig. 4B shows the long-term stability of this novel stationary phase after SiO₂ NPs coated μ GC columns were subjected to the 7.5 psi flow and 160°C temperature for 24 hours. Similarly, Fig. 5 demonstrates the time stability of NPs-based stationary phase after 15 injections on the μ MCC.

CONCLUSION

SiO₂ NPs coating fabricated by the LbL technique has been incorporated into μ GC separation columns and utilized as a new stationary phase for the first time. With simple and parallel fabrication procedures, LbL technique has shown the ability to generate homogenous conformal SiO₂ NPs coating with easy nanoscale thickness control inside the μ GC columns with different configurations. μ GC columns (both single and multi- capillary) with this stationary phase provided good separations of an alkane mixture with a wide range of boiling points.

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