HIGH DENSITY SEMIPACKED SEPARATION COLUMNS WITH OPTIMIZED ATOMIC LAYER DEPOSITED PHASES

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ABSTRACT

This paper reports the development of a new class of high-performance microfabricated separation columns called high-density semi-packed columns (HDSPCs). These columns are realized by using a meter long and 145 μm -wide silicon microchannel design with embedded circular micropillars (15 μm diameters) and 5 μm post spacing (perpendicular to the gas flow). The HDSPCs are coated using our previously developed atomic layer deposition (ALD) based aluminium oxide and silane functionalized thin adsorbent film. Moreover, in this study we optimize both ALD deposition temperature (100 ° C, 150 °C, 250 ° C and 300 ° C) and film thickness (10 nm, 20 nm and 30 nm) using different chromatographic parameters (plate number, peak-to-peak resolution, and separation factor). Additionally, the thermodynamic characteristics of these silane functionalized/ALD films are also studied using Van't Hoff plots. These columns with optimized stationary phases are able to provide $\approx 8,000$ effective plates/meter and

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successfully separate a custom made hydrocarbon sample mixture with high peak-to-peak resolution.

Keywords: Micro gas chromatography, separation column, stationary phase, atomic layer deposition.

I. INTRODUCTION

Microfabricated separation columns are produced using standard micromachining processes that selectively etch a silicon substrate; this is followed by sealing the etched silicon channels with a glass wafer. After which the sealed silicon microchannels are coated with either a polymer based liquid or solid-adsorbent thin films. The utilization of MEMS techniques for miniaturization of separation columns is an ongoing research area and dates back to 1979 when Terry and co-workers [1] fabricated 1.25 m-long, 200 μm -wide and 30- μm deep silicon columns. After wet etching, the columns were sealed with a glass wafer and coated with a liquid based stationary phase (OV-101). The condensation of stationary phase at corners and non-uniform film thickness lead to poor chromatographic performance. Following this in 1994, 90-cm long, 10- μm deep and 300- μm wide rectangular columns were fabricated by Reston and Kolesar [2]. Moreover, researchers at Sandia National Lab[3] developed separation columns with different channel dimensions from 10 μm to 80 μm -wide, 200 μm to 400 μm - deep and 10 cm to 100 cm-long using both wet and plasma etching techniques. These columns were etched anisotropically and channels with a spiral pattern were designed. Both static and dynamic coating techniques were used for coating OV1 based polymer stationary phases after performing anodic bonding. Although the film thickness was not uniform, columns were able to successfully separate a mixture of dimethyl methyl phosphate (DMMP) from

toluene and xylene. Agah *et al.* [4] introduced high performance rectangular separation columns with on-chip heaters and sensors for rapid temperature programming. In this work, 3 m-long, 150 μm -wide and 250 μm -deep etched-backed and dynamically coated columns were able to separate a complex 20 compound mixture in 5 minutes. Similarly, Reidy and coworkers [5] at the University of Michigan, Ann Arbor described an efficient procedure for statically coating rectangular silicon columns with dimethyl polysiloxane (PDMS). In this paper, the authors reported coating a 3 m-long separation column with a very thin (100 nm -200 nm) and uniform film to achieve high separation efficiency (12,500 theoretical plates). Although microseparation columns have been traditionally fabricated on a silicon wafer, Bhushan *et al.* [6] utilized a standardized LiGA (lithography, electroplating and molding) process to fabricate high-aspect-ratio nickel columns. In this study, 2 m-long, 50 μm -wide and 300 μm -deep metal columns were sealed using electroplating and statically coated with OV-1 polymer. Agah *et al.* [7] employed very innovative low-mass oxynitride films to realize 25 cm-long, 65 μm -semicircular buried separation columns. These columns provided 5000 plates/meter and showed better performance than a 50 μm fused silica capillary column. It is pertinent to mention that up until 2009 microfabricated columns were designed like an open channel configuration. For the first time Amin *et al.* [8] utilized MEMS techniques and introduced multicapillary columns (MCCs) to improve the separation efficiency and sample capacity. Two and four channel polymer coated MCCs (25 μm -wide) were produced to achieve high separation efficiencies of 12,500 plates/meter. Similarly, Mark Shannon's group at the University of Illinois at Urbana Champaign also utilized MEMS fabrication techniques to realize partially buried columns [9] with a rounded channel profile. The effect of different

channel geometries (circular-spiral, square-spiral and serpentine) on column performance was also characterized by the same group [10]. Meanwhile, the MEMS lab at Virginia Tech reported a unique microfabricated column design called “Semipacked Columns (SPCs)” [11]. In order to improve the sample capacity and velocity profile inside microchannels, the group skilfully integrated micropillars inside the fluidic channel. These columns provided superior chromatographic performance (10,000 plates/m) and sample capacity compared to their open-rectangular counterparts. More recently our group also introduced bi-directional variable width micro separation columns [12].

Although the miniaturization of separation columns generates a number of benefits but it also presents a number of technical fabrication challenges. One of these challenges being to be able to achieve uniform and reproducible stationary phase coatings especially for very small column dimensions. Similar to conventional capillary columns, microcolumns were initially coated with liquid polymer based thin films. The use of non-traditional adsorbent based coating method for microfabricated columns was reported by Robert E. Synovec’s group at University of Washington [13, 14]. The authors integrated single-walled CNTs into a 50 cm-long, 100 μm x 100 μm square microfabricated column. The growth of CNTs was carried out in-situ using a standard chemical vapor deposition technique. CNTs based solid stationary phase coupled with integrated resistive heaters enabled the ultrafast separation of a four compound mixture in less than a second. Moreover, the same group also introduced a thin film of monolayer-protected gold nanoparticles (MPN) as a stationary phase for both round and square shaped capillary columns [15-17]. Amin *et al.* further utilized thiol-functionalized gold layers as a stationary phase [18] for ultra-narrow single and multi-channel microfabricated columns.

This method was based on seedless electroplating techniques. Although requiring manual gold removal steps, this technique presented promising separation results and produced columns with 20,000 plates/meter.

Furthermore, Vial *et al.* employed MEMS compatible sputtering technique to deposit solid adsorbent materials like silica [19], graphite [20], and alumina [21] for open and semipacked columns. Additionally, our group integrated thin films (≈ 500 nm) of silica nanoparticles (SNPs) inside both 1m-long single channel columns (150 μm -wide and 250 μm -deep) and 25 cm-long MCCs (20 μm -wide and 220 μm -deep) using a well-established layer-by-layer coating method [22]. This highly stable and homogenous SNPs based stationary phase was able to separate a complex aromatic hydrocarbon mixture. Moreover, the enhancement of separation capability of CNTs and graphene functionalized PDMS stationary phases is recently reported for both open-tubular and semi-packed columns [23]. Atomic layer deposition (ALD) based coating, recently developed by our group for SPCs (1m-long, 190 μm -wide with 20 μm -circular micropillars and 20 μm -post spacing), also enables the realization of a highly reproducible, conformal, easy to use, mechanically and thermally stable separation films [24, 25]. This stationary phase deposition technique has been successfully employed by our group for a monolithically integrated separation and detection module [24] and a single chip GC system (injection, separation, and detection) [26]. A consistent research effort is also being made to use new fabrication techniques [27, 28], novel substrate and coating materials [29-32], on-chip fluidic interconnects [33], system level component integration [31, 34-39], and application-specific stationary phases [40, 41] to further enhance the capabilities of micro gas chromatography (μGC) system.

There are a number of publications related to SPCs but due to limitation of coating techniques all of the reported designs either utilized very lightly packed columns (micropillar post spacing $\geq 20 \mu\text{m}$) [42] or channels with shallow depths ($\leq 100 \mu\text{m}$) [19]. It has been well established (Van Deemter Equation) that the efficiency of separation columns can be enhanced by decreasing the column width. Therefore, the performance of SPCs could be further improved by reducing the effective channel width (reducing the micropillar diameters and spacing) provided a suitable stationary phase coating method exists. Due to the inherent properties of ALD, especially its highly conformal deposition, it holds a tremendous potential for coating the columns with very small features (below $\leq 10\mu\text{m}$ regime). In this report, we present high-density semipacked columns (HDSPCs), as shown in Figure 1, coated with optimized silane functionalized/ALD based stationary phases. The performance of ALD-based thin films is optimized using different deposition temperatures (100 °C, 150 °C, 250 °C and 300 °C) and thicknesses (10nm, 20nm, and 30nm).

II. EXPERIMENTAL

A. Column Fabrication

To demonstrate the wafer-level coating for HDSPCs architecture, we fabricated 1m-long, 145 μm -wide, 155 μm -deep HDSPCs with 10.5 μm circular posts and 7.5 μm post-spacing using standard MEMS processes. The fabrication of these columns is similar to our recently published work [25] and performed on a 4 inch-wide and 500 μm -thick single side polished silicon wafer. Briefly, the RCA cleaned wafer is first primed using HMDS followed by heating at 110 °C for 4 minutes. Afterwards AZ9260 photoresist is spin coated at 2000 rpm and the wafer is soft-baked at 110 °C for 90 seconds to get film

thickness of $\approx 8 \mu\text{m}$. An ultra violet light source is used to transfer the pattern from the mask onto the spin-coated wafer using a mask aligner (MA-6). Afterwards the wafer is first developed in a diluted AZ400K solution and then hard-baked for 4 minutes at 110°C . A standard BoschTM process [43] (source power 1800W with gas flow rates/pulse durations for $\text{SF}_6 = 300 \text{ SCCM}/5\text{s}$ and $\text{C}_4\text{F}_8 = 150 \text{ SCCM}/2.2\text{s}$) is used inside a deep reactive ion etcher (DRIE) to etch the hard-baked wafer to produce columns with a highly anisotropic etch profile and depth of $153 \mu\text{m} \pm 2 \mu\text{m}$ (sample size 12). The anisotropic etching was performed in two steps (each 25 minutes long) with backside of the wafer cooled down to -10°C . The channel depth is only limited by the under-cutting of micropillars (photoresist thickness after 50 minutes etching was $\approx 4.5 \mu\text{m}$). The final diameter of the micropillars measured using an SEM was $10.5 \mu\text{m} \pm 0.4 \mu\text{m}$ (sample size 12) which is less than the designed feature size of $15 \mu\text{m}$. In the next step, acetone is first used to clean the etched silicon wafer followed by an oxygen plasma cleaning step for 5 minutes. The use of oxygen plasma is twofold; first it removes the photoresist from the top silicon surface and finally it removes the passivation polymer (C_4F_8) inside the microchannels deposited during etching. It has been experimentally confirmed that the non-removal of this passivation polymer results in improper ALD-film deposition since the surface properties of the polymer are different from the silicon surface. Figure 2 shows the SEM images of a highly-packed etched silicon device after photoresist removal and plasma cleaning steps.

B. ALD Coating

The optimization of aluminum oxide film is carried out at different temperatures (Table 1) and thicknesses using trimethylaluminum (TMA) and water as precursors inside a thermal ALD chamber. Since the film deposition at lower temperatures takes a longer time, first the effect of change in chamber temperature is studied for a fixed film thickness (100 cycles and 10nm). It is important to note that the deposition rate for each recipe in Table 1 is around 1 Å/cycle. Each ALD deposition cycle consists of four steps, exposure of each precursor i.e. TMA and water for 15 ms (20 sccm flow) is followed by a purge cycle depending on the selected temperature. The increase in purge time for a low temperature (Table 1) is necessary to avoid the chemical vapor deposition of aluminum oxide film [44] which is due to the slow desorption rate of water at low temperatures.

C. Anodic Bonding and Silane Coating

Following wafer-level ALD coating, the etched silicon wafer is first diced into the individual devices, cleaned with water and then separately bonded with a Borofloat™ wafer at 380 °C and 1250 V for 45 minutes using a custom-made anodic bonding station. Following this deactivated fused silica glass capillary tubing (200 μm outer-diameter, 100 μm internal-diameter and 25cm-long) is attached to the inlet and outlet ports of each column using a two port epoxy adhesive. As demonstrated previously [19], the surface of ALD-aluminum oxide is not sufficient for chromatographic separations. Therefore, each column is filled with a solution of 10mM chlorodimethyloctadecylsilane (CDOS) diluted in toluene for surface functionalization. In the next step, each column is sealed at both ends using septa and kept at room temperature for typically 24 hours. Before performing any chromatographic experiments, columns are purged with dry nitrogen for 45 minutes to remove silane solution. Afterwards each column is conditioned inside a GC oven for

one hour from a room temperature to 150 °C (2 °C/min) with a constant nitrogen flow (7.5 psi). The yield of our coating technique is very high and close ≈ 90 % across different wafers (6 wafers and 24 fabricated devices).

III. RESULTS AND DISCUSSION

The effect of aluminum oxide deposition conditions on the chromatographic separations is studied in detail by first varying the chamber temperature (100 °C, 150 °C, 250 °C and 300 °C) and then the film thickness (10 nm, 20 nm and 30 nm). As a first step, the film thickness is fixed to 10 nm while the deposition temperature is varied using conditions mentioned in Table 1. It is important to note that it takes longer to deposit ALD-based films at lower temperatures. Different chromatographic parameters (Van Deemter plots, Van't Hoff plots, peak-to-peak resolution, separation factor, retention time and peak widths) are extracted from the chromatogram to benchmark the performance of each deposited film using n-nonane and n-decane (diluted in dichloromethane) as probes. An unretained methane gas vapor is used to measure the average carrier gas velocities and hold-up time (three sample points) against different inlet pressures for each ALD/silane functionalized column. Plate height (H) is considered to be the most important performance index for quantitative evaluation and optimization of a chromatographic system. H is given by L/N , where L is the length of a column and N is the plate number. Theoretically N is given by equation 1 and typically measured graphically from a chromatogram using equation 2 [45]

$$N = \frac{t_r^2}{\sigma^2} \quad (1)$$

$$N = 5.546 \times \left(\frac{t_r}{w_{1/2}} \right)^2 \quad (2)$$

Where, σ^2 represents the peak dispersion (band broadening), t_r is known as the retention time and $w_{1/2}$ is the peak width at the half height. The high packing density of HDSPCs result in the longer hold-up times compared to our previously reported lightly packed columns [25]. Therefore, the plate numbers (N) and plate height (H) cannot be true indicators of the column's separation power. Under this condition, a better approach to characterize the separation efficiency of the MEMS columns is to use the effective plate number (N_{eff}) as the figure of merit

$$N_{eff} = 5.546 \times \left(\frac{t_r - t_o}{w_{1/2}} \right)^2 \quad (3)$$

$$H_{eff} = \frac{L}{N_{eff}} \quad (4)$$

Where t_r is the retention time and $w_{1/2}$ is the peak-width at half height for n-decane diluted in dicholormethane. While t_o is the methane hold-up time. Figure 3 shows Van Deemter plots of HDSPCs with aluminum oxide film deposited at different temperatures. From these plots it is clear that film deposited at 300 °C provides the best performance (N_{eff} =8021 plates per meter) for the complete range of carrier gas velocities. The density of ALD film increases with the increasing growth temperature [46, 47]. For example, the density of Al_2O_3 film increases from 2.7 g/cm³ [47] to 3.5 g/cm³ [46] by increasing the growth temperature from 100 °C to 350 °C respectively. The reduction in density of resulting Al_2O_3 film at lower temperature could be attributed to a higher concentration of the hydroxyl (OH) groups on the surface [46] and/or a higher film porosity. The increased concentration of hydroxyl groups (at lower temperatures) in turn provides more active

sites for silane functionalization. Both mechanisms result in increasing the surface area for solute-film interaction. The effect of surface roughness of the film on chromatographic performance will be comparatively negligible. The AFM measurements from previous studies show that the surface roughness remains below 5 Å for Al₂O₃ films grown at low (177 °C [46]) and high (300 °C [25]) temperatures. A more insightful look into the plots presented in Figure 4 also demonstrate that the adjusted retention time ($t_r - t_o$) for the films deposited at lower temperature is larger (due to higher solute-film interaction), while films deposited at higher temperatures provide narrower chromatographic peaks resulting in an overall high efficiency and peak-to-peak resolution. Therefore, these results demonstrate the higher retention behavior of the films grown at lower temperature.

Thermodynamic properties of silane functionalized aluminum oxide films were also evaluated using Van't Hoff plots (Figure 5). The linear plots ($R^2 > 0.99$) are generated between 35 °C to 80 °C using n-decane (diluted in dichloromethane) as a probe and dead-time is calculated from an unretained methane vapor. From these plots, the standard adsorption heat ($|\Delta_r H^\theta|$) for silane functionalized ALD-films deposited at different temperatures is calculated, they range from 41.4-45.6 $k \cdot J/mol$ (universal gas constant $R = 8.31445 \text{ J/mol}$ [48]). The results show that all these films show similar retention behavior and are thermodynamically very similar. These values are close to higher surface area CNTs ($|\Delta_r H^\theta| = 45.6 \text{ k} \cdot J/mol$) based coatings, deposited using chemical vapor deposition and also using n-decane as a probe [13]. Moreover, other chromatographic parameters such peak-to-peak resolution (R_S), separation factor between the two adjacent hydrocarbon analytes (n-nonane and n-decane) are also evaluated

$$R_S = 2 \times \left(\frac{t_{rb} - t_{ra}}{w_{rb} + w_{ra}} \right) \quad (5)$$

Where, t_{ra} and t_{rb} correspond to retention times and w_{ra} and w_{rb} represent the peak widths at the base of the corresponding compounds a and b. Table 2 shows the complete list of these extracted parameters (average values, sample size 3) for four different HDSPCs, each with a 10 nm film deposited at four different temperatures. It is clear from the results (Table 2) that the best chromatographic performance (N_{eff} and R_S) is achieved when ALD-film is deposited at higher temperature (300 °C). The deposition at 300 °C provides an additional advantage of taking the least time (≈ 13 minutes). After the optimization of deposition temperature, the next step is the optimization in the film thickness (10 nm, 20 nm, and 30 nm) which is carried out using the same performance parameters. Table 3 shows the summary of these results and it is clearly demonstrated that 10 nm film deposited at 300 °C shows the best overall chromatographic performance. Moreover, the kinetic, thermodynamic and retention behavior of 30 nm film deposited at 300 °C (taking 39 minutes to deposit) is very similar to the 10 nm film deposited at 100 °C (240 minutes).

One can deduce important characteristic of columns by using reduced variables such as the reduced plate height ($H_{reduced}$) [45]. The reduced plate height is defined as

$$\text{Open Capillary Columns: } H_{reduced} = \frac{H_{eff}}{d} \quad (6)$$

$$\text{Packed Columns: } H_{reduced} = \frac{H_{eff}}{dp} \quad (7)$$

Where d is the diameter of an open capillary column and dp is the particle size for a packed column. For open tubular capillary columns the $H_{reduced}$ ranges between 1 and 1.7, while for the packed column it ranges from 10 to 17. In order to characterize our micro fabricated HDSPCs, we are going to use both expressions (6) and (7). The micro column channel is designed with the effective column width of 40 μm and the pillar diameter of 15 μm (Figure 1). Moreover, the optimum value of H_{eff} for our columns is $\approx 125 \mu\text{m}$ (10 nm film deposited at 300 °C). By using these numeric values, the $H_{reduced}$ values for our columns are 3.12 (6) and 8.33 (7). From these numbers, it is clearly demonstrated here that these micro columns do not have any conventional counter parts.

The importance of fast chromatographic analysis especially for portable GC systems could not be overstated. The GC column should be operated close to the minimum plate height (preferably at higher flow rates) to achieve fast separations. One of the main advantages of semi-packed columns compared to open tubular columns include a small loss in plate efficiency at higher flow rates [49, 50]. The minimum loss in plate efficiency at higher linear gas velocities is also observed for HDSPCs (plots in Figure 3 are flat at high velocities). We also plotted (Figure 6) Giddings-Golay (f_1) and Martin-James (f_2) gas compression coefficients [51, 52] as a function of retention factor for n-nonane. The gas compression coefficient f_1 increases as the head pressure at column inlet is increased, conversely the coefficient f_2 decreases. Both plots for f_1 and f_2 in Figure 6 show that the retention factor of n-nonane increases from 1.26 to 1.36 and saturates at higher inlet pressures values. Both Figures 3 and 6 confirm that we can achieve faster analysis with HDSPCs without significantly reducing plate efficiency or retention factor.

A test mixture containing a nine hydrocarbon mixture was prepared to test the separation capability of the HDSPCs with ALD enabled alumina stationary phase. HDSPC with ALD coating successfully separates this custom made test mixture at isothermal conditions (50 °C, 37.5 psi and 100:1 split ratio) as shown in Figure 7. Moreover, HDSPCs were also tested using a straight chain and a high boiling point custom made alkane mixture (diluted in n-hexane) as shown in Figure 8. The total separation run time for the current set of columns for the alkane mixture (n-decane to n-heptadecane) is comparable to our earlier columns coated with ≈ 500 nm silica nanoparticles based stationary phases [22]. It is worth to mention that even with HDSPCs, we are unable to separate the highly volatile gases (methane, ethane, propane, and butane) at room temperature.

The performance of HDSPCs (≈ 8000 plates/m) is significantly better than our previously presented results for 1 m-long semi-packed columns with 20 μm integrated circular micropillars and 40 μm post-spacings (≈ 4000 plates/m) [25]. In both studies, the columns were coated under similar ALD coating conditions (10 nm ALD film at 300 °C) with silane. Although the plate number for ALD-coated HDSPCs is lower than the semi-packed columns dynamically coated with OV1 stationary phase (≈ 15000) [49]. But the fabrication yield of current work ($\approx 90\%$) is significantly higher than the dynamically coated semi-packed columns. For comparison purposes, we also tried to coat HDSPCs with traditional dimethyl polysiloxane (OV1) based stationary phases using both static and dynamic coating techniques. We were unable to pass solution through HDSPCs even after reducing the concentration of OV1 in n-pentane from 10 mg/mL to 1 mg/mL. Similarly, due to very narrow channel dimensions, other thin film coating techniques

developed by our group (LbL self-assembly of SNPs [22] and gold thiol-based stationary phases [53, 54]) could not be used for HDSPCs. Therefore, the use of high-yield ALD-silane based method not only presents an easy route towards the development of separation columns with very narrow channels (even smaller than 5 μm) but also provides a wafer level and semiconductor process compatible technique for the realization an integrated μGC chip [24, 26].

IV. CONCLUSIONS

This research allowed us to introduce a new generation of semi-packed columns with a high packing density. Our recently introduced high-yield ALD/silane functionalized coating scheme is integrated with these HDSPCs to provide the chromatographic separation capabilities. The coating is further optimized by varying both the deposition temperature (100 °C, 150 °C, 250 °C, and 300 °C) and the film thickness (10 nm, 20 nm, and 30 nm). The best chromatographic performance is generated by a 10 nm aluminum oxide film deposited at 300 °C. Moreover, this optimized film also yields the highest peak-to-peak resolution and peak capacity.

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Figure 1: Channel profile of a 1m-long high density semipacked column (HDSPC).

Figure 2: SEM images of HDSPCs after dry etching (a) top view, (b) cross-section.

Figure 3: Van Deemter plots for HDSPCs with 10 nm ALD/silane functionalized film deposited at different temperatures. The error bars in the plot are smaller than symbols therefore they are omitted (sample size 3).

Figure 4: Adjusted retention time (a) and peak-width at half height (b) plots for HDSPCs with 10 nm ALD/silane functionalized film deposited at different temperatures.

Figure 5: Thermodynamic properties (Van't Hoff plots) of silane functionalized aluminum oxide films deposited at different temperatures using. *n*-decane is used as a probe with each column tested from 35 °C to 80 °C at 12 cm/sec. Methane vapor is used to calculate the dead times/capacity factors (k') corresponding to different temperatures with $R = 8.31445 \text{ J/K}\cdot\text{mol}$. The error bars in the plot are smaller than symbols therefore they are omitted (sample size 3).

Figure 6: Giddings-Golay (f_1) and Martin-James (f_2) gas compression coefficients as a function of retention factor for the best performing HDSPC (coated with 10nm ALD film at 300 °C). Dashed lines are drawn as a guide for the eye.

Figure 7: Separation performance of an ALD-coated/silane functionalized HDSPCs at 50 °C. Compound identification in order of elution 1.dichloromethane 2. n-hexane 3. benzene 4. toluene 5. tetrachloroethylene 6. chlorobenzene 7. ethylbenzene 8. p-xylene 9. n-nonane

Figure 8: Separation performance of an ALD-coated/silane functionalized column using a custom made straight chain alkane mixture diluted in *n*-hexane. Compound identification in order of elution 1. *n*-decane 2. *n*-undecane 3. *n*-dodecane 4. *n*-tridecane 5. *n*-tetradecane 6. *n*-pentadecane 7. *n*-hexadecane 8. *n*-heptadecane (0.1 μ L injection, 100:1 split ratio, temperature programming from 75 $^{\circ}$ C to 150 $^{\circ}$ C at rate of 70 $^{\circ}$ C /min).

Table 1: Deposition conditions for 10 nm thick aluminum oxide film deposited at different temperatures using TMA and H₂O as precursors.

10 nm aluminum oxide ALD film growth from H₂O and TMA at different temperatures				
Cycle	100 °C	150 °C	250 °C	300 °C
H₂O (ms)	15			
Wait (s)	60	20	5	4
TMA (ms)	15			
Deposition time (minutes)	200	32	17	13

Table 2: Different chromatographic parameters extracted from GC testing of HDSPCs with 10 nm aluminum oxide film grown at four different temperatures. The underlined values in the table represent the minimum value for HETP and the maximum values for the remaining parameters.

10 nm film deposited at	HETP^{min} (cm)	N_{eff} (max) (plates/m)	Optimum Velocity (cm/sec)	Peak-to-peak Resolution^{max} (C₉-C₁₀)	Separation Factor (k_{n+1}/k_n)	ΔH (kJ/mol)
100 °C	0.022	4381	13.18	21.79	2.43-2.53	44.87
150 °C	0.019	5214	13.61	22.54	2.4-2.5	41.39
250 °C	0.017	5654	12.61	24.49	2.47-2.58	45.68
300 °C	<u>0.012</u>	<u>8021</u>	15.91	<u>28.4</u>	2.38-2.53	43.29

Table 3: Different chromatographic parameters extracted from GC testing of HDSPCs with aluminum oxide film grown at 300 °C with three different thicknesses (deposition time in minutes). The underlined values in the table represent the minimum value for HETP and the maximum values for the remaining parameters.

Thickness (deposition time)	HETP _{min} (cm)	N _{eff} (max) (plates/m)	Optimum Velocity (cm/sec)	Peak-to-peak Resolution _{max} (C ₉ -C ₁₀)	Separation Factor (k _{n+1} /k _n)	ΔH (kJ/mol)
10 nm (13 min.)	<u>0.012</u>	<u>8021</u>	15.91	<u>28.4</u>	2.38-2.53	43.38
20 nm (26 min.)	0.018	5424	13.26	24.28	2.44-2.55	43.88
30 nm (39 min.)	0.023	4347	13.51	21.86	2.58-2.60	43.81