

Fabrication of micropreconcentrator devices for trace level gas sensing

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Abstract

Micro gas chromatograph sensors have recently been developed which allow for the development of portable sized gas sensors. In order to improve the minimum level of detection for these, micropreconcentrators can be employed to increase the concentration of trace level gasses in the sample. In this work, a micropreconcentrator has been designed and fabricated in silicon. COMSOL Multiphysics was employed to develop and analyze the fluid flow and heat transfer properties of the device. A microchannel with an array of 50 μm diameter, cylindrical pillars was etched into silicon using deep reactive ion etching to form a channel with a high surface area to volume ratio. Carbon nanotubes were grown using plasma enhanced chemical vapor deposition inside the etched channel as an adsorbent material. The channel was bonded with a cover wafer to form a hermetically sealed chamber. A gold resistive heater with 300 nm thickness with a 15 nm titanium adhesion layer was deposited on the backside of the wafer to allow for thermal programmed desorption.

1. Introduction

The ability to measure gases, especially volatile organic compounds, at trace level has been shown to have new importance recently. Research into industrial monitoring, health sciences, and national security has demonstrated need for the ability to detect trace level gasses quickly and accurately. However, this sensing has previously been limited to on site sampling which is then tested at an external laboratory. While this testing method provides accurate data, it has an extremely limited sample rate and has a significant delay between obtaining sampling and results. Thus, extensive, mobile testing is extremely limited.

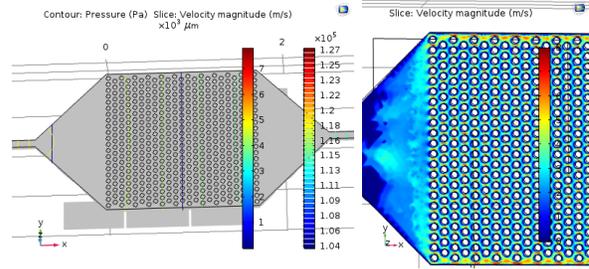
In order to address this issue, various miniaturized gas sensors have been developed. However, these devices often have higher detection thresholds than the equipment currently in use. In order to improve the measuring properties of these devices micropreconcentrator devices have been fabricated. Micropreconcentrators lower the level of detection by adsorption and controlled desorption of certain gasses. In typical function, a measured volume of sample gas is passed through the preconcentrator, causing certain trace level gasses adsorb to the material in the preconcentrator. The sample gas feed is then disengaged, and a carrier gas is passed through the preconcentrator while the preconcentrator is heated. The heating thermally desorbs the trace level gasses, which then pass to the gas sensor. The volumes of initial sample gas and carrier gas can then be used to determine the concentration of the trace level gas in the original sample¹.

This summer, we designed and developed a process for fabricating a micropreconcentrator from a silicon chip. DRIE was used to form the micropreconcentrator channel on a silicon wafer. A liftoff procedure was used to pattern an integrated heating element onto the backside of the wafer. Carbon nanotubes were selected for the adsorbent material as they have been shown to have good properties of adsorption and desorption, especially for volatile organic compounds². Catalyst for carbon nanotube growth is sputtered into the etched channel, and carbon nanotubes are grown using plasma enhanced chemical vapor deposition. The channels are then sealed by bonding another wafer to the etched wafer.

2. Experimental Procedures and Results

A. COMSOL Multiphysics

COMSOL Finite Element Modeling software was used to develop and analyze the design of the preconcentrator prior to manufacture. A general design of sloping inlets and outlets with an array of micro pillars to increase the surface area to volume ratio was decided upon to lower the pressure drop across the device while still providing ample surface area for adsorption and even flow distribution. The computational fluid dynamics (CFD) function of COMSOL were employed for this analysis, using an assumption of laminar flow through the device. Various height to length ratios were tested with a fixed depth to determine the optimal shape.

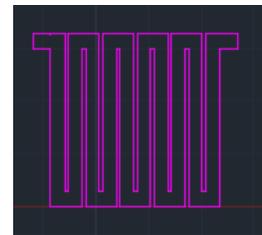


(left) COMSOL simulation of the pressure drop across the preconcentrator, (right) COMSOL simulation of the velocity profile through the device

Based on the CFD results, a design with equal height to length ratios was selected. The results showed a generally even distribution without excessive velocity gradients. COMSOL gave a pressure drop across the device of approximately 3 psi, although this does not compensate for the roughness of the sidewalls when coated with carbon nanotubes. The design was then transferred to a two dimensional design file using AutoCAD™ software for fabrication.

B. Heater fabrication

The formation of the resistive heating element was performed first. A liftoff procedure was used to pattern the heater. To perform the liftoff procedure, a negative photoresist (NR9-1500p, Futurrex Productivity Tools) was spun onto the wafer to create a photoresist layer. The photoresist was then exposed using a maskless aligner (Heidleburg Instruments MLA 150) and the heater portion of the previously developed two dimensional design file with a light wavelength of 375 nm and a dosage of 650 mJ/cm². After exposure, the photoresist was developed with RD6 developer. The wafer was descummed using reactive ion etching (RIE) (Oxford End-point RIE). The surface was then metalized using electron-beam physical vapor deposition (CHA Industries Mark 40), depositing 15 nm of titanium (Ti) as an adhesion layer and 300 nm of gold (Au) as the resistive heating element. After metallization, the wafer was soaked in acetone for 6-12 hours and sonicated for 1-2 hours in order to complete the liftoff procedure. The results of the liftoff procedure were then analyzed using an optical microscope.

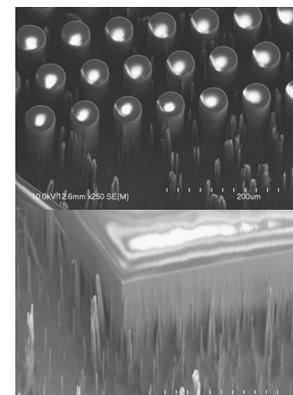


Resistive heating element design in AutoCAD™

C. Microchannel formation

Microchannel formation was achieved through deep reactive ion etching of the opposite side of the channel. The wafer was patterned with SPR 220-7.0 photoresist. The photoresist was spun onto the wafer and exposed using the same maskless aligner as before. The photoresist was then left overnight to rehydrate before developing with MF-319 developer. The channel was then etched to a depth of 250 μm using a deep reactive ion etching Bosch process (STS HRM ICP). The main channel is 5 x 5 mm² and the sloping inlets having an angle of 90°.

The results of the etching are shown to the right. The top photo shows the micropillars and the bottom image shows the sidewall of the channel. As shown in the photos, a high aspect ratio was achieved with nearly vertical sidewalls. Small, thin vertical structures were also created with the etching. These may be the product of residual photoresist in the channel after development. This fabrication issue may be fixed with



SEM images of the (top) etched pillars and (bottom) channel wall

increased exposure dosage, a longer development time, and a descum process may be used to prevent this from reoccurring.

D. Carbon nanotube growth

Carbon nanotube growth was developed through plasma enhanced chemical vapor deposition. Growth was tested on a catalyst layer of 5 nm iron with 100 nm Ti used as an adhesion layer as developed by Tsu-Hsuan Chang. For the purpose of the tests, catalyst was deposited onto a wafer and plasma enhanced chemical vapor deposition (PECVD) (Aixtron Black Magic) was used to grow the carbon nanotubes. Acetylene was used as the growth gas with ammonia used as the diluting gas. This sample was analyzed using SEM (Hitachi S-4700 FE-SEM) characterize the growth of the CNTs.

3. Conclusion and Future work

Thus, over this summer we worked towards fabricating a preconcentrator device which uses CNTs as the adsorbent material. A design was developed and tested using COMSOL Multiphysics. A liftoff procedure was employed to pattern an integrated heating element. A channel was etched with deep reactive ion etching into the silicon channel. Catalyst for CNT growth was sputtered and CNT growth tested with PECVD tested.

Future testing of the micropreconcentrator will be performed finalize the fabrication and to investigate the performance of the micropreconcentrator. These tests will characterize the performance of the micropreconcentrator with regards to its gas testing capabilities. The breakthrough volume (the point of saturation for adsorption material), and the breakthrough velocity (the point at which the gases fail to adsorb in the preconcentrator) will be measured, as well as the preconcentration factor (testing concentration / sample concentration).

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