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SEPARATION AND DETECTION OF TOXIC GASES WITH A SILICON MICROMACHINED GAS CHROMATOGRAPHY SYSTEM

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Abstract

A miniature gas chromatography (GC) system has been designed and fabricated using silicon micromachining and integrated circuit (IC) processing techniques. The silicon micromachined gas chromatography system (SMGCS) is composed of a miniature sample injector that incorporates a 10 µl sample loop; a 0.9-m long, rectangular-shaped (300 µm width and 10 µm height) capillary column coated with a 0.2-µm thick copper phthalocyanine (CuPc) stationary-phase; and a dual-detector scheme based upon a CuPc-coated chemiresistor and a commercially available, 125-µm diameter thermal conductivity detector (TCD) bead. Silicon micromachining was employed to fabricate the interface between the sample injector and the GC column, the column itself, and the dual-detector cavity. A novel IC thin-film processing technique was developed to sublime the CuPc stationary-phase coating on the column walls that were micromachined in the host silicon wafer substrate and Pyrex® cover plate, which were then electrostatically bonded together. The SMGCS can separate binary gas mixtures composed of parts-per-million (ppm) concentrations of ammonia (NH_3) and nitrogen dioxide (NO_2) when isothermally operated (55-80°C). With a helium carrier gas and nitrogen diluent, a 10 µl sample volume containing ammonia and nitrogen dioxide injected at 40 psi (2.8×10^5 Pa) can be separated in less than 30 minutes.

Introduction

Gas chromatography (GC) is a popular analytical chemistry tool commonly employed in the laboratory setting to analyze gas mixtures. With a GC system, the components of a gas mixture can be separated, identified, and their concentrations quantified. In their most common configuration, GC systems tend to be large, fragile, expensive, and bulky pieces of instrumentation. In consonance with the Environmental Protection Agency (EPA) and National Institute of Occupational Safety and Health (NIOSH) federal mandates for accomplishing on-site chemical analyses, several investigators have recently focused their attention toward realizing portable and robust GC systems[1-10]. Consistent with this motivation, this research realized a functional GC system by applying conventional integrated circuit (IC) processing techniques in conjunction with the concept of micromachining the column and integrating the key components on a single-crystal silicon wafer. The evolution of this technology will ultimately afford the opportunity to realize a complete miniaturized GC system that is inherently smaller, less massive, and highly portable compared to the presently available hardware (envisaged to be similar in size to a pocket calculator).

As depicted in Figure 1, the silicon micromachined gas chromatography system (SMGCS), consistent with conventional gas chromatography systems, consists of five fundamental components: (1) carrier gas supply, (2) sample injection system, (3) separation column, (4) detector, and (5) data processing element. In this research, the separation column and detector were microfabricated. To separate the components of a gas sample, a precise and reproducible volume needs to be extracted from the environment of interest with the sample injection valve, where it is then injected into the capillary column via an inert carrier gas. The stationary-phase thin-film which coats the surfaces of the capillary column adsorbs and desorbs each component of the sample gas depending upon its unique activation energy.

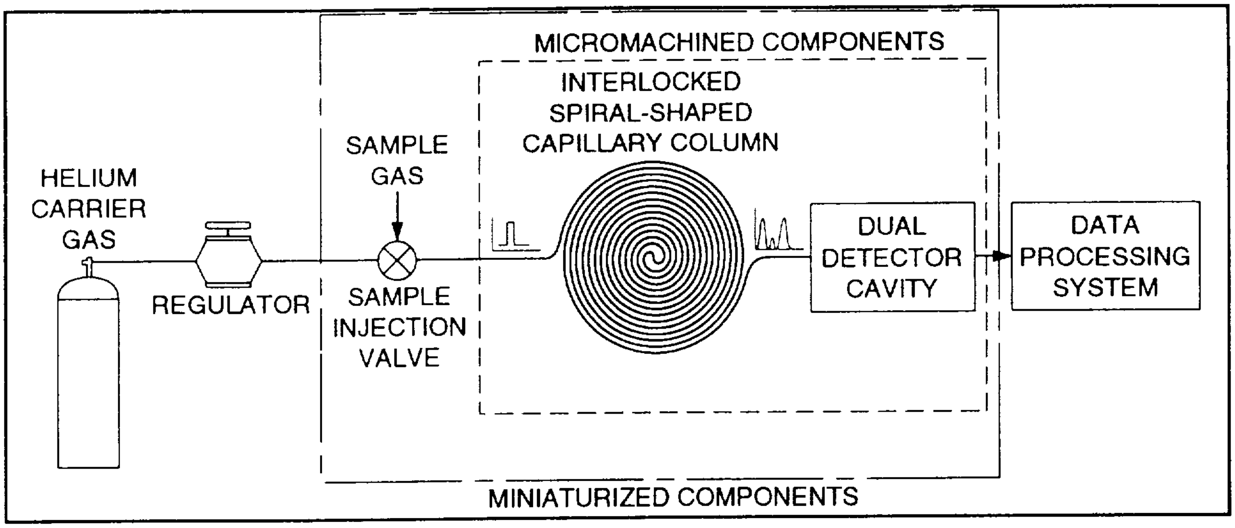


Figure 1. Functional block diagram of the micromachined gas chromatography (GC) system.

The differential propagation rate (velocity) of each gas component through the capillary column depends upon several factors, including the sample injection pressure, carrier gas velocity, the temperature, and the affinity of the individual gas components relative to the column's thin-film stationary-phase. As a consequence of this phenomenon, the gas components comprising the injected sample pulse mixture emerge at the capillary column's output as a time-resolved series of peaks that are separated from each other in the inert carrier gas. To detect the peaks associated with each separated gas component, the capillary column's gas effluent is analyzed by one or more detectors, whose functions are to measure a particular property of the gas components (for example, thermal conductivity, electrical conductivity, etc.). The magnitude of a detector's response to a particular gas component can correspondingly be related to its concentration in the injected sample.

SMGCS Design and Fabrication

In this research, a commercially available, electronically-actuated sample injector (Valco Instruments Company, Inc., product E6N6W, Houston, TX) incorporating a sample loop with a 10 μl volume was utilized to satisfy the critical requirement for injecting a reproducible pulse of the sample gas into the GC column. The volume of the sample loop was established experimentally by analyzing the conditions under which the capillary column would become saturated if it were to be filled with the highest conceivable concentration of any of the analyte gas components.

As shown in Figure 1, the miniaturized portion of the SMGCS is composed of a micromachined, interlocking, spiral-shaped capillary column integrated with a dual-detector arrangement, which consists of a separately batch fabricated copper phthalocyanine (CuPc) coated integrated circuit (IC) chemiresistor and a commercially available, 125-μm diameter thermal conductivity detector (TCD) bead (Thermometrics, Inc., model B05, Edison, NJ). The lower portion of the micromachined GC column is fabricated in a 3-inch diameter (100)-oriented silicon wafer (Polycore Electronics, *n*-type, Newberry Park, CA), and the matching upper portion of the column is etched in a 4-inch square Pyrex® cover plate (Schott America, Pyrex® 7740, Yonkers, NY). Before these two components are electrostatically bonded together, the GC column walls are coated with an α-phase CuPc thin-film[11], and then the TCD is mounted in the micromachined detector cavity. The independently batch fabricated IC chemiresistor (MOSIS - Metal-Oxide-Semiconductor Implementation System, Marina del Rey, CA) is coupled with the SMGCS along with the interface structure for the sample injector. The electrical response of the SMGCS results from the fundamental gas chromatography process which occurs in the separating column, and the corresponding performance of the non-specific TCD and the highly-specific CuPc-coated chemiresistor.

To quantify the efficiency of a candidate GC column design, a *separation factor* (*SF*) performance parameter can be calculated based upon the following equation[12]:

$$SF = \frac{L}{h(D, z_o, v_o, k)g}\left(\frac{k}{k+1}\right)^2 \tag{1}$$

where L is the column's length, k is the column's partition ratio, g is a pressure correction factor, and h is the theoretical plate height. The theoretical plate height, h, is further defined by[13]:

$$h = 2\frac{D}{v_o} + \frac{4(1+9k+51k^2/2)}{105(1+k)^2}\frac{v_o z_o^2}{D} + \frac{2k^3}{3(1+k)^2}\frac{v_o z_o^2}{F^2 c^2 D_1} \tag{2}$$

where D is the diffusivity of the sample gas in the mobile phase, v_o is the effluent output velocity, z_o is the column height, F is the ratio of the effective surface area of the stationary-phase relative to the actual area, c is the partition coefficient, and D_1 is the diffusivity of the stationary-phase. The numerical values and relationships utilized in the design of the SMGCS are summarized in Tables 1 and 2.

Table 1. Fundamental Micromachined Gas Chromatograph Design Relationships.

GC System Operational/Performance Parameter	**Analytical Relationship**
Plate Height	$h = 2\frac{D}{v_o} + \frac{4(1+9k+51k^2/2)}{105(1+k)^2}\frac{v_o z_o^2}{D} + \frac{2k^3}{3(1+k)^2}\frac{v_o z_o^2}{F^2 c^2 D_1}$
Partition Ratio	$k = k_o e^{(-E_a/k_b T)}$
Partition Coefficient	$c = k / F$
Diffusion Coefficient (Gas)	$D = \frac{v_{av}\lambda}{2}$
Output Velocity	$v_o = \frac{z_o(P_i^2 - P_o^2)}{6\mu L P_o}$
Pressure Correction Factor	$g = \frac{9\left[\left(\frac{P_i}{P_o}\right)^4 - 1\right]\left[\left(\frac{P_i}{P_o}\right)^2 - 1\right]}{8\left[\left(\frac{P_i}{P_o}\right)^4 - 1\right]^2}$

Table 2. Physical, Operational, and Experimental Parameters for the Silicon Micromachined Gas Chromatograph Design.

Physical Parameters		
Parameter	***Symbol***	***Value***
Boltzmann's Constant	k_b	1.38 x 10^{-23} joules/Kelvin
Helium Viscosity	μ	200 poise
Diffusion Coefficient	D	10^{-6} m^2/sec
Mean Free Path	λ	5 x 10^{-9} m
Average Molecular Velocity	v_{av}	400 m/sec
Operational Parameters		
Parameter	***Symbol***	***Value***
Input Pressure	P_i	40 psi (2.8 x 10^5 Pa)
Output Pressure	P_o	1 atmosphere (1 x 10^5 Pa)
Column Length	L	0.9 m
Column Width	Y	300 μm
Column Height	$2z_o$	10 μm
Temperature	T	80 °C
Column Permeability	q	2.6 x 10^7 poise/m^2
Pressure Correction Factor	g	1.08
Experimental Parameters		
Parameter	***Symbol***	***Value***
Heat of Adsorption	E_a	0.38 eV
Partition Ratio Constant	k_o	4 x 10^{-4}
Adsorption Lifetime	$1/\beta$	93 sec
CuPc Diffusion Coefficient	D_1	6 x 10^{-19} m^2/sec
Partition Coefficient	c	2400
Effective Surface Area Ratio	F	14
Crystallite Radius	r_{cr}	300 Å
Crystallite Height	h_{cr}	2000 Å

The critical component in the SMGCS is the micromachined capillary gas separation column, which is 0.9-m long and has a rectangular-shaped cross-section (300 μm width and 10 μm height). The aspect ratio of the capillary column's cross-section was designed using the analytical model developed by Golay[13] in conjunction with the limitations imposed by the IC photolithography and wet chemical etching processes. As depicted in Figure 2, the silicon wafer portion of the column was fabricated using conventional IC negative photoresist (Olin Hunt Specialty Products, Inc., Waycoat HR100 negative photoresist, West Patterson, NJ), an SiO_2 etch mask, and wet chemical isotropic etching

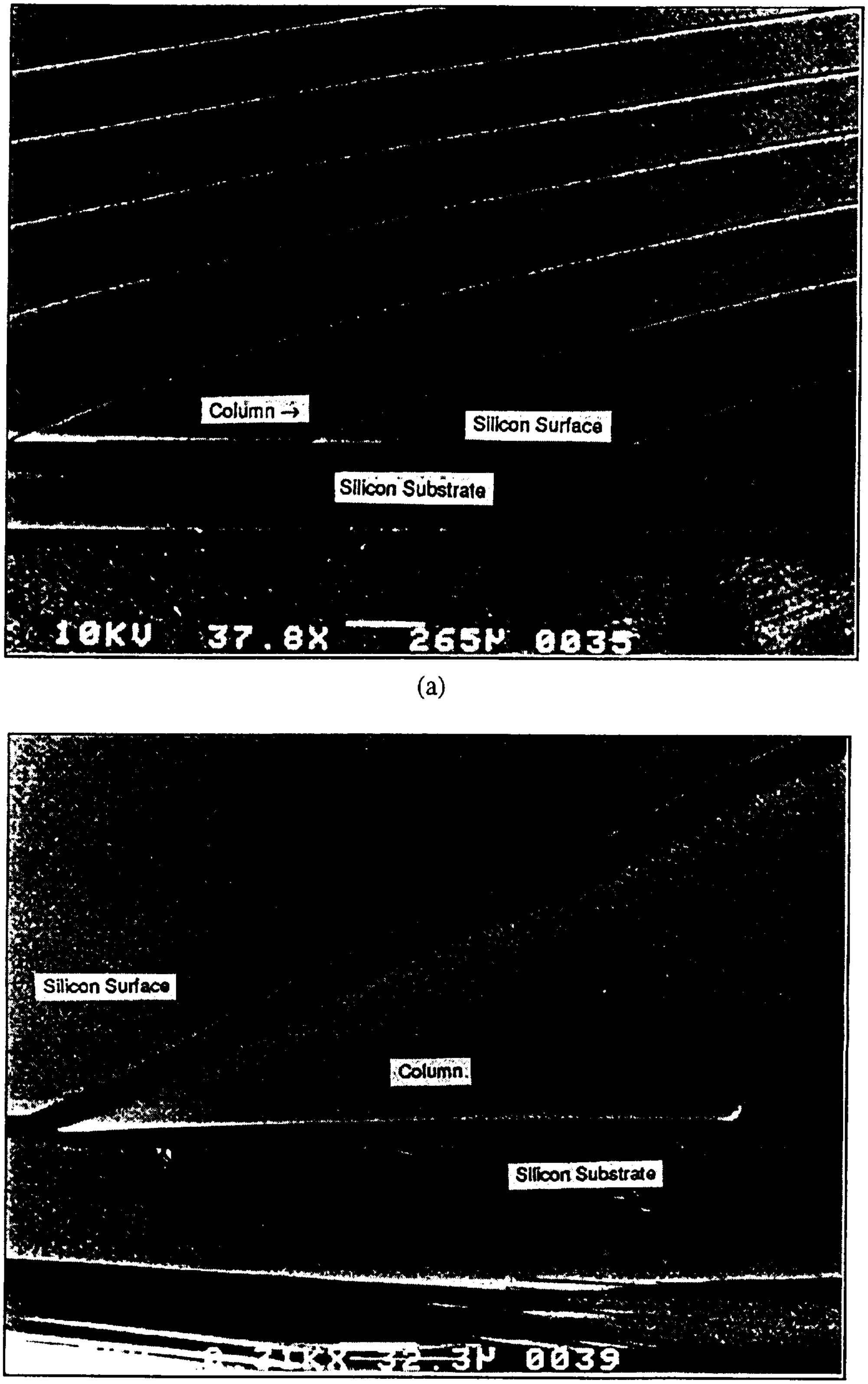


Figure 2. Scanning electron microscopy (SEM) micrograph of the isotropically etched portion of the GC capillary column micromachined in the silicon wafer (300 μm width and 9 μm depth). (a) expanded view. (b) detailed view.

($HF:HNO_3:CH_3COOH$, 2:15:5). The height of the column patterned in the silicon wafer was 9 μm. The balance of the column's height (1 μm) was correspondingly etched in the Pyrex® cover plate with a buffered hydrofluoric acid solution ($HF:NH_4F$, 1:4). Before depositing the column's CuPc stationary phase and electrostatically bonding the two components together, the silicon wafer was anisotropically etched (20 % wt KOH at 50 °C) to realize the injection port interface structure (Figure 3) and the dual-detector cavity (Figure 4), which was designed to maximize its performance by minimizing its dead volume (20 nl dead volume after the TCD was positioned).

The SMGCS column's CuPc (Fluke Chemical Corporation, Ronkonkoma, NY) stationary-phase (0.2 μm thickness) was sublimed (3 Å/sec deposition rate) under vacuum [He cryo-pumped, 10^{-6} Torr (1.3×10^{-4} Pa)] onto the surfaces of the etched silicon wafer and Pyrex® cover plate (Denton Vacuum, Inc., model DV-602, Cherry Hill, NJ). As shown in Figure 5, a commercially available polishing medium (PSI Testing Systems, Inc., 0.3 μm Al_2O_3 particle size, product number 16.3-6, Houston, TX), lubricated only with deionized water (to minimize contaminating the CuPc thin film) and secured on a marble plate, was used to selectively remove the CuPc thin film from the surfaces of the silicon wafer and Pyrex® cover plate, while leaving behind the desired stationary-phase on the column walls. The morphology of the resulting α-phase CuPc column coating was verified with scanning electron microscopy (SEM), transmission electron microscopy (TEM), and transmission electron diffraction (TED). Infrared (IR) spectroscopy was independently utilized to verify the chemical structure of the deposited CuPc coating (after deposition and after it was mechanically polished) and to investigate the selective adsorption of the ammonia (NH_3) and nitrogen dioxide (NO_2) analytes.

After the TCD was mounted in the dual-detector cavity, the silicon wafer and Pyrex® cover plate were electrostatically bonded[14] together (1800 V, 150 °C, 24-hour duration). The CuPc-coated chemiresistor was then aligned with its port on the dual-detector cavity. To complete the SMGCS fabrication, the sample injector (Figure 3) was connected to the column's input port with a short length (20 cm) of micro-capillary tubing (794 μm o.d., 254 μm i.d.; Valco Instruments Company, Inc., product T20N10D).

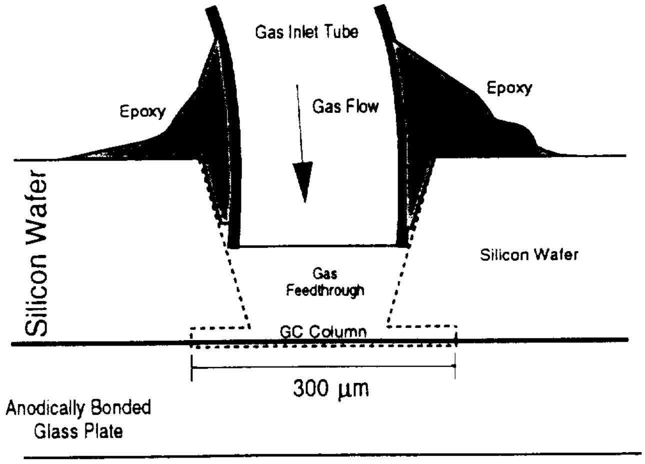


Figure 3. Side view of the anisotropically etched injection port interface structure design.

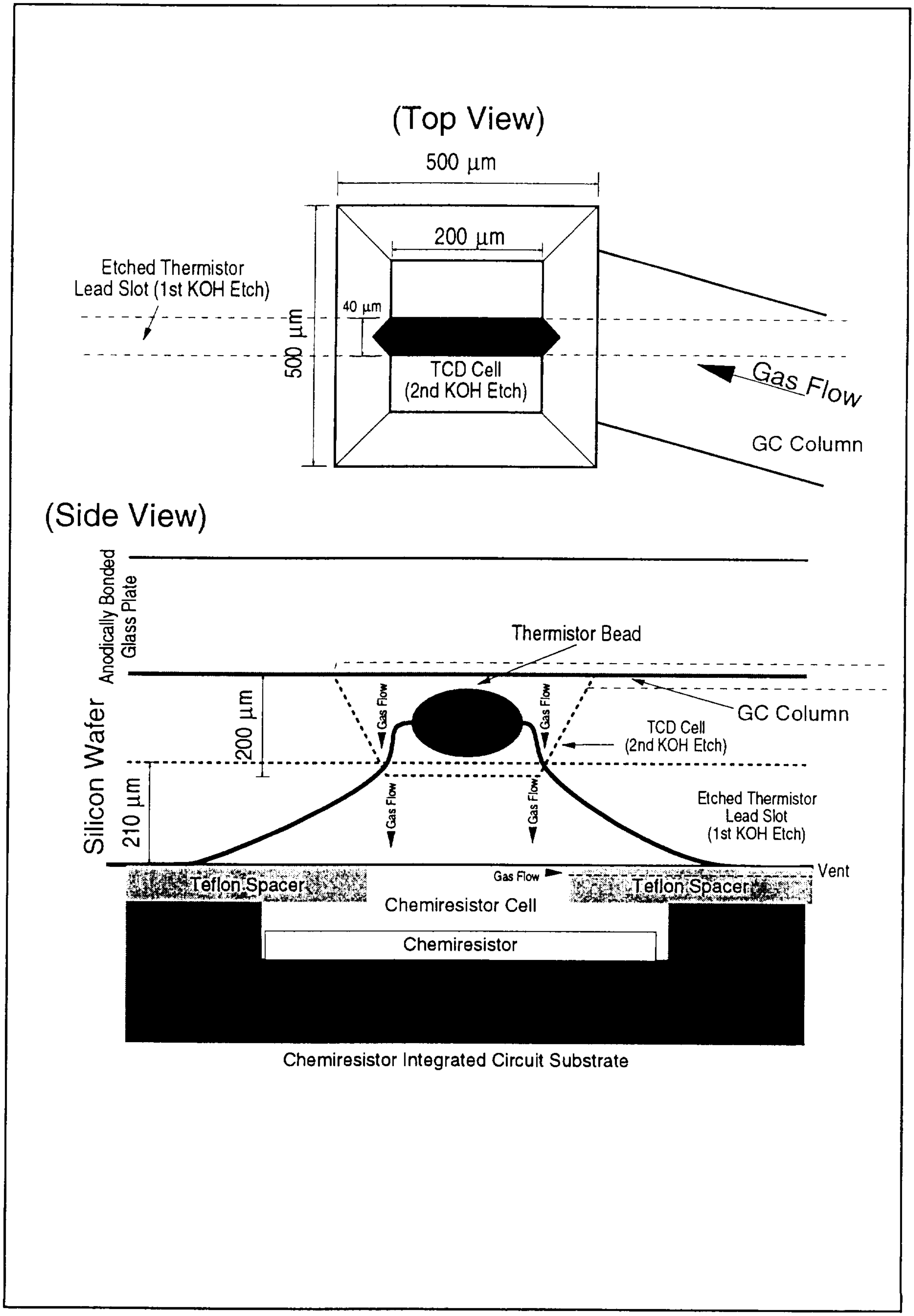
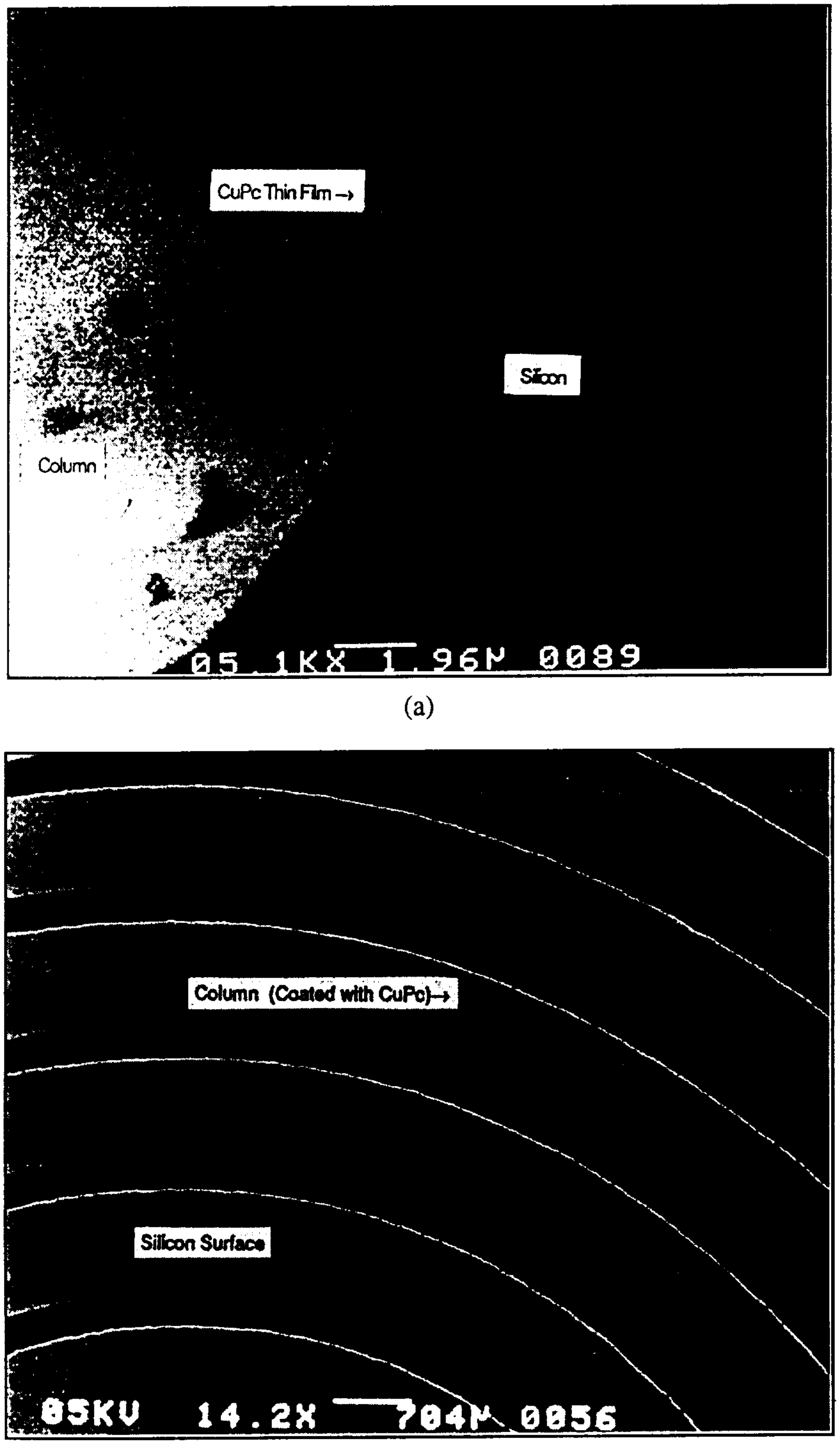


Figure 4. Thermal conductivity detector (TCD) cell and chemiresistor interface design.



(a)

(b)

Figure 5. SEM micrograph of the CuPc-coated portion of the GC column micromachined in the silicon wafer. (a) Column before the CuPc coating was removed from the flat surface regions (intra-column) of the silicon wafer. (b) Column after the CuPc coating was removed from the flat surfaces required to accomplish the electrostatic bonding process with the Pyrex® cover plate. (Similar results are achieved with the portion of the capillary column etched into the Pyrex® cover plate).

SMGCS Performance Evaluation

To evaluate the efficiency and separating power of the SMGCS, helium was used as a carrier gas, and binary mixtures of parts-per-million (ppm) concentrations of ammonia (NH_3) and nitrogen dioxide (NO_2) were realized using commercially available permeation tubes (GC Industries, Inc., models 23-7014 and 23-7052, Fremont, CA) and nitrogen (N_2) as the diluent. The 10 µl gas sample volumes were injected into the column with a pressure of 40 psi (2.8 x10^5 Pa) to maximize its theoretical separation factor[13]. To maintain the integrity of the electrostatic bond between the silicon wafer and the Pyrex® cover plate, isothermal operation of the SMGCS was limited to temperatures spanning 55 °C to 80 °C. In operation, the TCD was used to capture the diluent nitrogen gas peak, and since the gas specific, CuPc-coated chemiresistor behaves as an integrating detector, its response was differentiated to establish the peaks associated with NH_3 and NO_2. Since NH_3 is an electron-donor gas, and NO_2 is an electron-acceptor species, their converse electrical interactions with the chemiresistor's *p*-type CuPc semiconductor coating motivated generating chromatograms that depict the absolute value of the detector's differentiated response (to facilitate their interpretation consistent with the format of conventional GC data).

Under isothermal operating conditions, Figures 6 and 7 illustrate the performance of the SMGCS to separate and detect NH_3 and NO_2 when their concentrations are systematically varied. Isothermal operation at 80 °C requires less than 30 minutes to process a gas sample. Using the numerical data summarized in Tables 1 and 2, along with equations (1) and (2), the theoretically calculated separation factor (SF), as shown in Table 3, agrees reasonably well with the values extracted from the measured chromatograms.

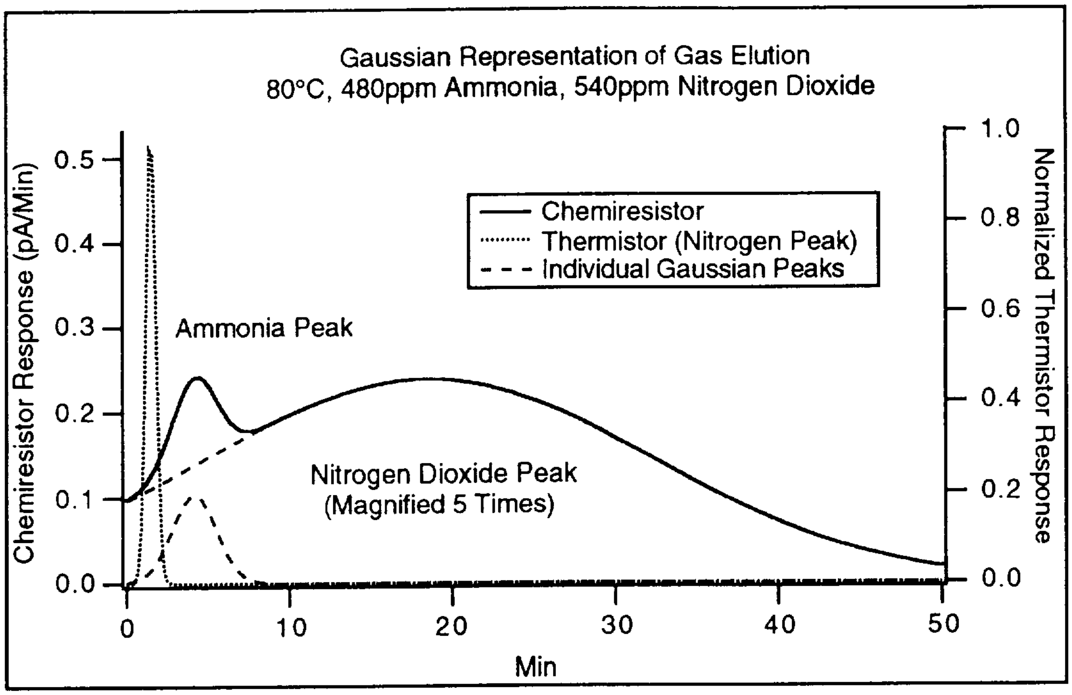
Table 3. Comparison of the SMGCS Theoretical and Experimental Values of the Separation Factor (SF).

Operating Temperature (°C)	**Theoretical SF**	**Experimental SF**
55	4.4	3.8
66	3.3	3.4
76	2.8	2.7
80	2.1	1.9

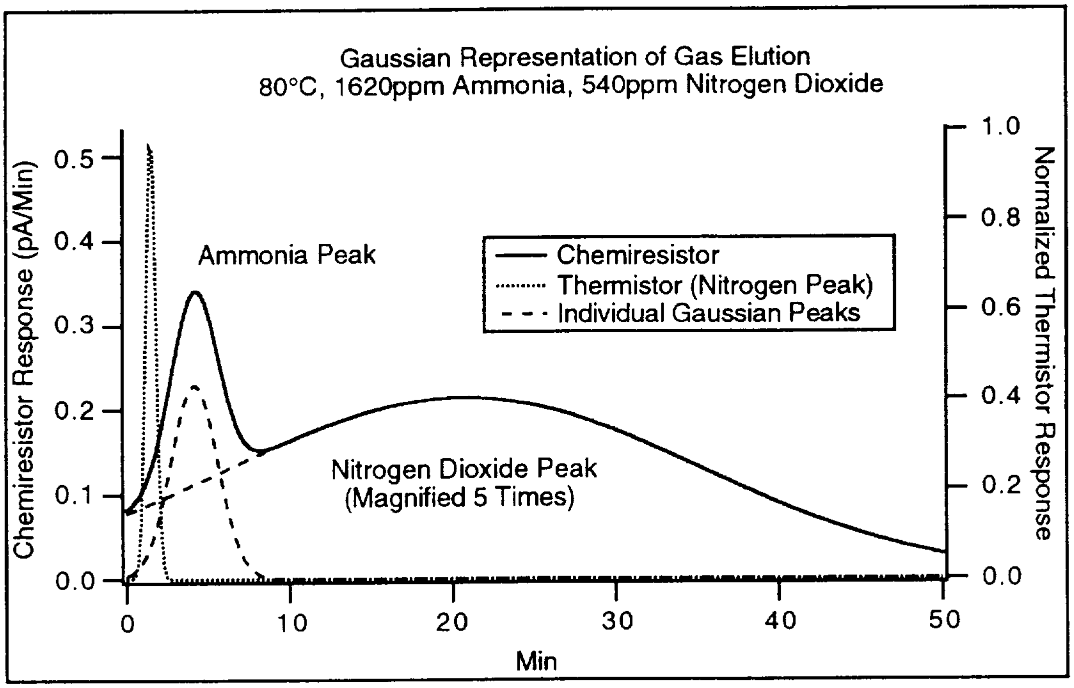
Conclusion

The results of this investigation demonstrate the viability of using single-crystal silicon micromachining for implementing a GC system and using a CuPc thin-film stationary-phase which is capable of separating and detecting NH_3 and NO_2. The significant accomplishments ascertained from this research can be summarized in two areas: micromachining and chemical sensing.

In the micromachining area, a novel TCD cell design was implemented. The critical features of this design, compared to those previously reported[1-3], include: reduced dead volume (less than 20 nl), ease of thermistor insertion, and the ability to pass the column effluent to another detector (e.g., the chemiresistor). Also, a new technique was developed, enabling, for the first time, the deposition of a nearly-homogeneous thin-film stationary-phase (2000 Å thick) within the micromachined GC column. Finally, the ability to perform a low temperature (less than 300°C) anodic bond (1800 V for 24 hours)

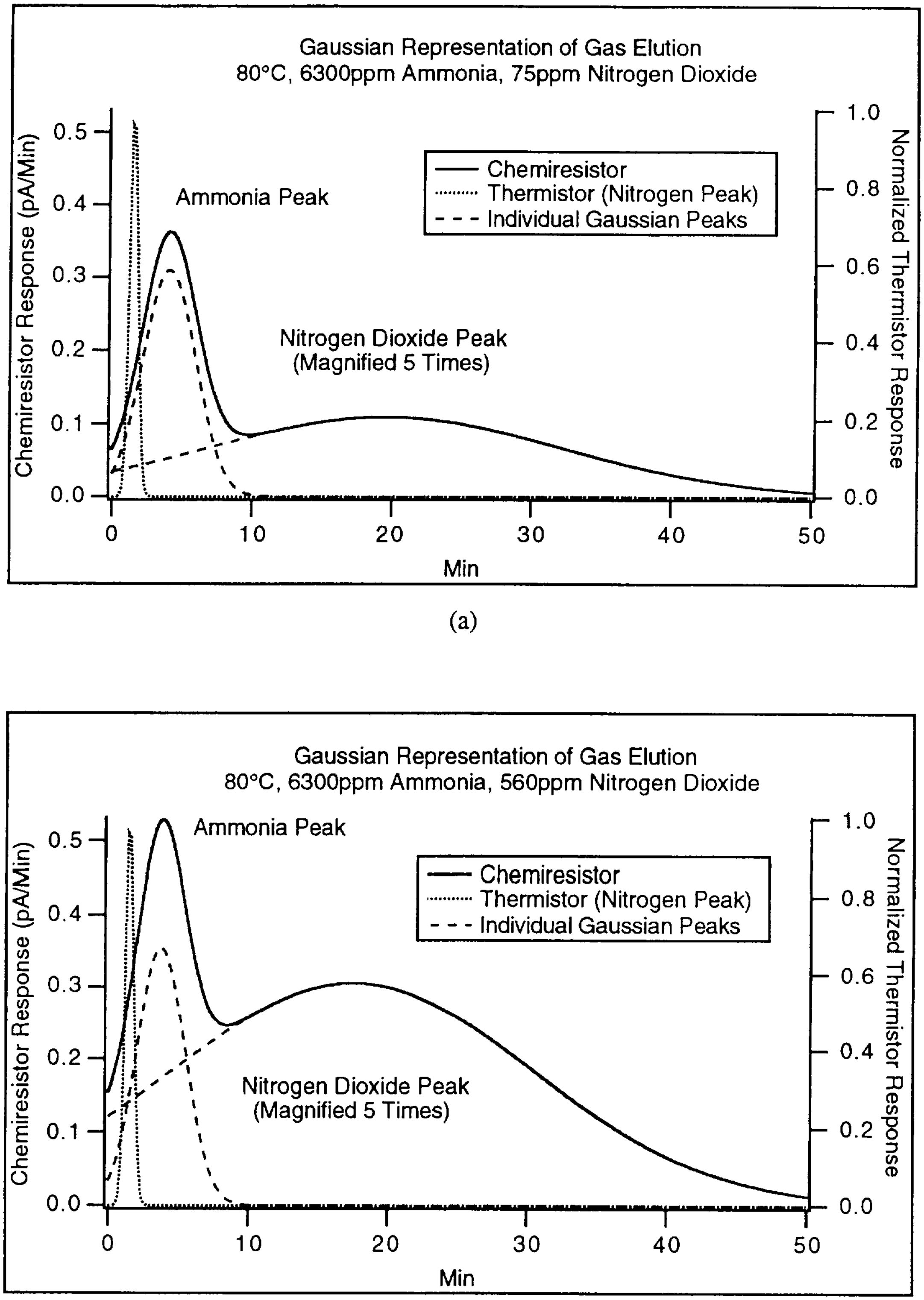


(a)



(b)

Figure 6. Chromatograms obtained with the micromachined GC system operated at 80 °C for two different NH_3 concentrations for a fixed NO_2 concentration (540 ppm). (a) 480 ppm NH_3. (b) 1620 ppm NH_3.



(a)

(b)

Figure 7. Chromatograms obtained with the micromachined GC system operated at 80 °C for two different NO_2 concentrations for a fixed NH_3 concentration (6300 ppm). (a) 75 ppm NO_2. (b) 560 ppm NO_2.

was demonstrated, which is inherently important because it is compatible with the thermally-sensitive thin films and other bulk materials.

The primary accomplishment was the separation and detection of NH_3 and NO_2. The SMGCS was capable of separating NH_3 and NO_2 at parts-per-million concentration levels in less than 30 minutes when operated at 80°C. Furthermore, this research served as a proof-of-concept for using a SMGCS to investigate the adsorptive properties of other thin films.

With respect to future research, improvements are being implemented concerning the column design and detector configuration. The micromachined GC column's length can readily be increased by decreasing the inter-column spacing without significantly sacrificing yield, resulting in a proportional increase in the separation factor (SF). Also, incorporating the chemiresistor IC directly within the detector cell, similar to the cavity specifically micromachined for the TCD, should improve the sensitivity of the chemiresistor (a smaller dead volume implies a higher localized analyte concentration). An integral heater (with controller) and micromachined sample injection valve could also be incorporated into the SMGCS design using standard IC fabrication techniques, further reducing the requirement for external equipment. Finally, investigations concerning the adsorptive properties of other thin films (in particular, other metal-doped phthalocyanines), using the SMGCS as a tool, should be of significant value to those developing chemical sensors based upon these materials.

Acknowledgments

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