A High Performance Hand-Held Gas Chromatograph

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April 28, 1998

Abstract

The Microtechnology Center of Lawrence Livermore National Laboratory has developed a high performance hand-held, real time detection gas chromatograph (HHGC) by Micro-Electro-Mechanical-System (MEMS) technology. The total weight of this hand-held gas chromatograph is about five lbs., with a physical size of 8″ x 5″ x 3″ including carrier gas and battery. It consumes about 12 watts of electrical power with a response time on the order of one to two minutes. This HHGC has an average effective theoretical plate of about 40k. Presently, its sensitivity is limited by its thermal sensitive detector at PPM.

Like a conventional G.C., this HHGC consists mainly of three major components: 1) the sample injector, 2) the column, and 3) the detector with related electronics. The present HHGC injector is a modified version of the conventional injector. Its separation column is fabricated completely on silicon wafers by means of MEMS technology. This separation column has a circular cross section with a diameter of 100 μm. The detector developed for this hand-held GC is a thermal conductivity detector fabricated on a silicon nitride window by MEMS technology. A normal Wheatstone bridge is used. The signal is fed into a PC and displayed through LabView software.

Introduction

Gas chromatography (GC) has proven to be a reliable method for identifying unknown chemical mixtures. In a GC, an unknown chemical mixture is first injected and carried by a carrier gas into its separation column. In the separation column, the chemical mixture is distributed between two phases, one a mobile phase and the other the stationary phase. The mobile phase is transported by a carrier gas in the separation column, and the stationary phase is adsorbed into a solid from the flowing mobile phase. Based upon the kinetics of the adsorption-desorption process in the gas-solid interface in the column, different chemicals achieve different moving speeds in the carrier gas. Within a precise column length, the chemical mixture can be separated into various components and recorded by the detector. For the conventional GC, detector sensitivities are at about parts per million for thermal sensitivity detectors and parts per billion for various ion cell detectors. Chemical components are identified through their retention times – the traverse time for each of them as they pass through the separation column.

The separation efficiency of the G.C. column is related to the degree to which a solute band broadens (which is a function of the width of the peak, w) relative to the length of time the band requires to traverse the column (its retention time t_R). The number of theoretical plates n is defined as [1],

$$n = 16 \, (t_R/w)^2 \qquad ---- \qquad (1)$$

Or, the number of effective theoretical plates is defined as,

$$N = 5.56 \, [(t_R - t_M)/w_{1/2}]^2 \qquad ---- \qquad (2)$$

where t_M is the duration for nonabsorbed gases to traverse the separation column and $w_{1/2}$ the half linewidth of a signal peak. The efficiency of a separation column is measured by the number of theoretical plates per unit length or the "height equivalent to a theoretical plate" h (HETP),

$$h = L/n \qquad ---- \qquad (3)$$

Or, the "height equivalent to one effective theoretical plate" H (HEETP),

$$H = L/N \qquad ---- \qquad (4)$$

In the conventional GC, the separation column is usually formed by a glass capillary with a diameter ranging from 150 to 300 microns and a length of around 100 meters. The values of h or H are on the order of millimeters. To achieve this high column efficiency, the temperature of the separation

column needs to be uniform. It must to be placed in a large, well- insulated oven. Because of this, conventional GCs are bulky, have high power consumption and are slow in response.

The hand-held GC should have a wide appeal for numerous applications, such as toxic gas monitors, pollution detectors, reaction gas analysis, and law enforcement usage. To miniaturize a conventional G.C. we first need to miniaturize its separation column and oven assembly.

The separation column and oven assembly can be greatly simplified when made from a highly thermal conductive material. Silicon has higher thermal conductivity than glass, and its surface under ambient conditions will naturally form silicon dioxide, an inert material which is ideal for forming the inner liner of the separation column. To form a highly efficient separation column on a silicon wafer, the column must have (a) a circular cross section, (b) an extremely smooth inner surface and (c) proper diameter in term of its length. The heater can then be made directly on the same silicon wafers or on a separate one.

Because of the small sample size, the thermal conductivity detector needs to be extremely sensitive. The heat capacity of the heater and the total amount of conductive heat loss other than that due to the carrier gas has to be minimized. This device is small so it can allow for the direct interconnecting of the thermal detector into the gas stream. All this is done by MEMS technology.

Fabrication Technology

Separation Column

Initially, a mask must be designed for the separation column. Column fabrication is limited to a 3" silicon wafer. The total length of the spiral column, is limited. Therefore, to have a reasonably high resolution or large number of theoretical plates, the diameter of the column needs to be small and precise. The finished column diameter is 100 microns. The length is about 5.6 meter. Since we are using an isotropic wet chemical etching technique to form the final column, the initial width of the spiral on the mask is 10 microns. With alignment fiducial marks, two masks which are mirror-images are made. In Fig. 1, the fabrication process schedule is listed.
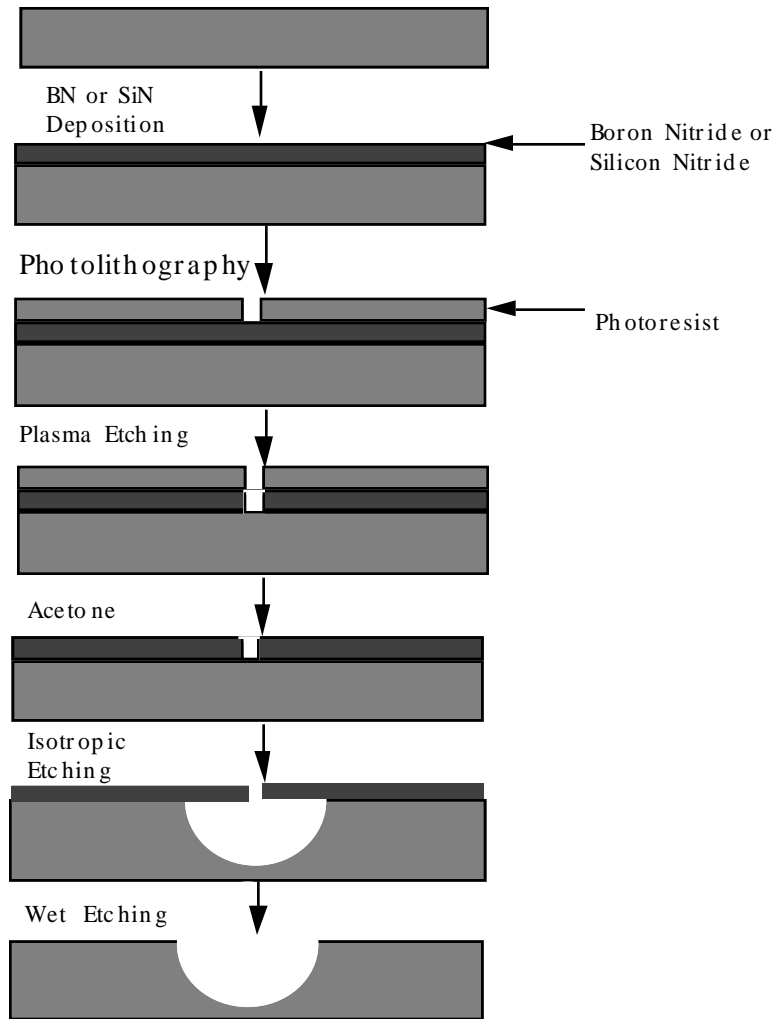
Process Schedule for Microchannel

Fig. 1 Process for Microchannel

Here, the mask pattern is shown to be formed onto a silicon nitride coated silicon wafer through a photolithographic process. A fine pattern is then etched through the silicon nitride with plasma. Afterwards, a semi-circular groove is etched into the silicon wafer through an isotropic wet chemical etching process.

The isotropic etching process, Fig. 2, for silicon is the $HF-HNO_3-CH_3COOH$ recipe.
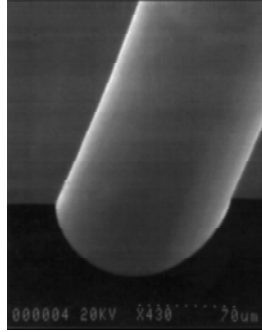
Fig 2 Semicircular Channel

However, silicon nitride can also be etched by this same etching process. This is due to the hydrofluoric acid (HF). If the etching time is short, a thick silicon nitride coating may be used. In this etching system, the oxidizing agent nitric acid (HNO_3) supplies both holes and hydroxyl groups to oxidize the silicon with the trace impurity of nitrous acid (HNO_2) in the solution[4,5,6,7].

$$HNO_2+HNO_3+H_2O \longrightarrow 2HNO_2+2OH^-+2h^+ \qquad (1)$$

$$4OH^-+4h^++Si \longrightarrow SiO_2+2H_2O \qquad (2)$$

The fluoride from the hydrofluoric acid (HF) will then combine with the silicon dioxide (SiO_2) to form the soluble solution H_2SiF_6.

$$SiO_2+6HF \longrightarrow H_2SiF_6+2H_2O \qquad (3)$$

Therefore, the overall net reaction is,

$$6HF+2HNO_3+Si \longrightarrow H_2SiF_6+2HNO_2+2H_2O \qquad (4)$$

The overall net reaction can generate nitrous acid (HNO_2), which promotes a reaction (1). Thus, the overall reaction is autocatalytic. The role of the acetic acid (CH_3COOH) is to dilute the etching reaction to be more controllable.

After the two wafers are fabricated, they are ready for bonding. Silicon fusion bonding, also known as silicon-to-silicon bonding, is the joining together of two silicon wafers without the use of intermediate adhesives such as

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polymers or melting glasses, and without the use of applied electric fields as in anodic bonding [9]. The bonding of two oxidized wafers at room temperature and subsequent annealing is the basic process, which allows the fabrication of buried oxide layers, and only standard silicon processing equipment is required.

Wafer Alignment and Bonding

Accuracy in etching the alignment V- grooves is essential. The groove width, location and alignment to the crystal plane is achieved during photolithography. Two wafers with mirror images of etched semicircular, continuous spiral channels, are aligned by the V-grooves on the wafer surface. Precision fibers are inserted into the V-grooves. The fibers are slightly oversized to prevent contact of the wafer surfaces. When the wafers are aligned, the wafer centers are pressed to make contact. The fibers are then removed. The bonded wafers are annealed to 1100^0 C for two hours. The bonded wafer pair is inspected under a UV lamp to detect internal voids (Fig 3, 3a).
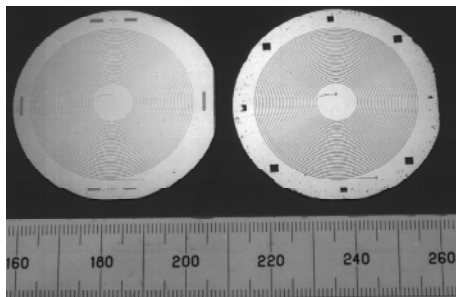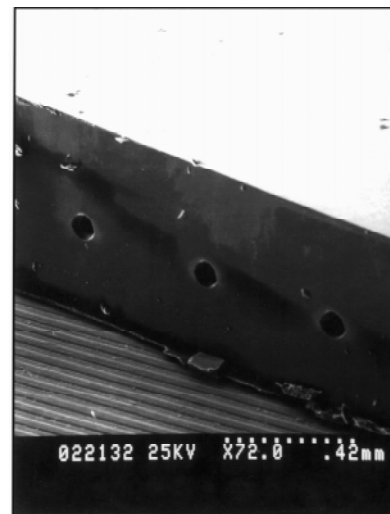

Fig. 3 Silicon Wafer Pair

Fig. 3a Bonded Silicon Wafer Pair

Column Coating and Conditioning

After the column is formed, it is ready for coating. The column needs to be clean from acid or base residues left in the column channel. This is done by pumping through a large volume of deionized (16 Meg Ohm) water. Afterwards, the column is inserted into the thermal oxide furnace (800^0 C) for one hr. to deposit a thin layer of oxide on the capillary column surface. The cleaned column is now ready for coating. A syringe filled with Dimethyl

silicone and chloroform solution is pumped through the column. The column is conditioned at 200^0 C with a flowing of N_2 for .5 hr, then, 100^0 C for .5 hr, then, 50^0 C for four hours.

Thermal Conductivity Detector

Silicon nitride has low heat conductance [$3.2x10^{(-2)}$ W/cm*K] and it can be made strong in a thin window structure. By forming a nickel resistance pattern on a silicon nitride window, a very sensitive, miniature thermal conductivity detector is created. Fig. 4 lists the standard process of forming a silicon nitride window and the process of forming a nickel resistance pattern by standard liftoff process.
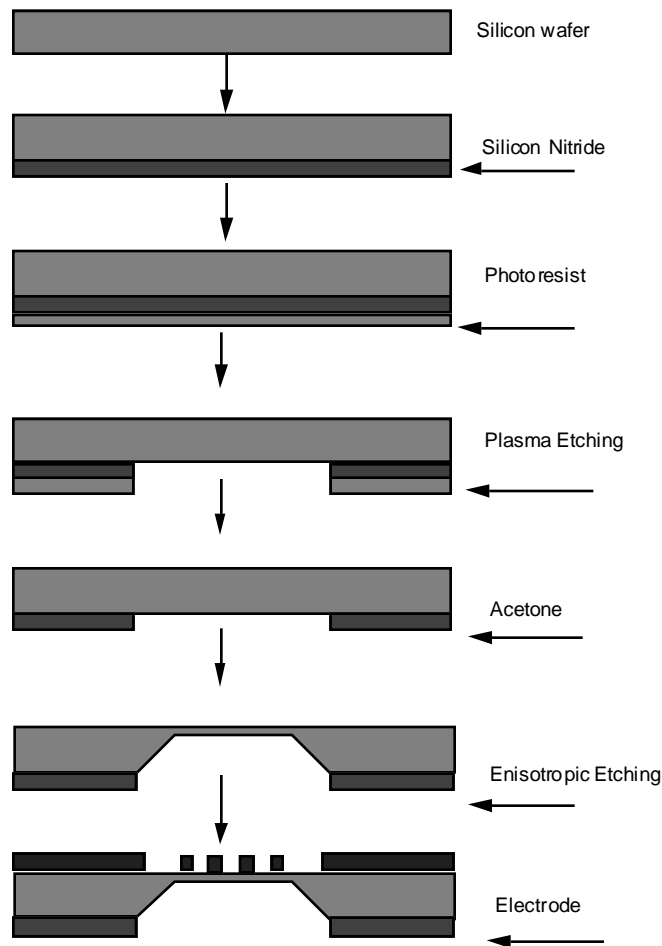
Thermal Conductivity Process Procedures

Fig. 4 Fabrication Process for the Thermal Conductivity Detector

Assembly

The basic chromatograph consists of three main components; 1) the sample injector, 2) the capillary column, and 3) the detector and related electronics. Because of the short retention time in the separation column, a fast gas sample injector is required. This is achieved by modifying a conventional injector. The injector is then interconnected with our innovative capillary GC column, and our highly sensitive micromachined thermal conductivity detector. The signal is detected with a Wheatstone bridge and amplified and processed through an on-board 386 /33 MHz microcomputer. The signal is then displayed on the screen through LabView software.

Tests and Results

With a head pressure of Helium carrier gas at 6 psi, the temperature of the column was set at 65 degrees Celsius. A sample gas with about 10 parts per million of C(1) to C(6) gases was injected. A series of differential signals was displayed on the screen as shown in Fig. 5.
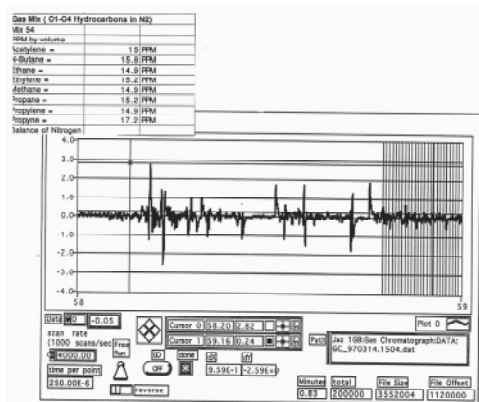

Fig. 5 Chromatogram

The traverse duration tm of a nonabsorbed gas was measured at about 8 seconds. The average retention time of the group tr was about 45 seconds. The average half linewidth $w_{1/2}$ is about 0.4 second. Therefore, the number of effective theoretical plates can be calculated. From equation (2),

$$N = 5.56 \; [(t_R - t_M)/w_{1/2}]2 = 4 *10^{\wedge}(4).$$

By equation (4), we can calculate the "height equivalent to one effective theoretical plate" H (HEETP),

$$H = L/N = 0.14.$$

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Discussion

The miniature silicon GC was initiated at Stanford University by S. C. Terry[2,3]. In this case, all three main components (injector, column, detector) were integrated on a bonded silicon–glass wafer pair. LLNL decided to microfabricate the three main components individually so that each can be optimized for high performance, small size, and ease of manufacture. The smooth inner surface and circular cross-section of the separation column together with seamless bonding between silicon wafers ensure precise uniform column coating. It is this uniform coating along with the high thermal conductivity of silicon which directly decides the selectivity and the resolution of the column. On the other hand, the temperatures of the injector and the detector normally need to be set higher to prevent condensation. These components need to be separated or thermally insulated from the separation column. System size reduction causes faster analysis response time, but sample volume reduction effects the detection sensitivity. A highly sensitive thermal conductivity detector is developed to compensate for the small sample size. This detector allows for sensitivity at the PPM level. In the near future, we intend to develop a sample preconcentrator and more sensitive detectors to enhance the detection sensitivity to the PPB region.

Acknowledgment

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