Silicon Components for Gas Chromatograph

Łukasz Nieradko[1], Krzysztof Małecki[2]
Wroclaw University of Technology, Institute of Microsystems Technology
Janiszewski Str. 11/17, PL-50372 Wrocław
[1]lunier@wtm.ite.pwr.wroc.pl
[2]malk @wtm.ite.pwr.wroc.pl

Abstract. The silicon-glass micromachined capillary column, dosing (sampling) valves and mass flow-meter for gas chromatograph are presented. The test structures have been fabricated and tested. A concept of new hybrid integrated model-scale portable gas chromatograph has been proposed.

Keywords: Chromatography, Micromechanics, Microsystems, Sensors, Silicon, Valve

1. Introduction

Gas and liquid chromatography is one of the most approved methods of chemical analysis. The variety of possible analysis (and their quality) is so high that it is almost sure that the method will be applied for many succeeding years. Miniaturisation of chromatographs enables extension of their application range. Introduction of fast, portable analysers in the chemical industry permits real time analysis of composition and monitoring of endangered places (like methane mines), which in effect improves work safety and quality of resulted products. The idea of integrated silicon chromatograph was born in 1979, when Terry [1] proposed the chromatograph integrated on 2“ silicon substrate, based on a gas chromatograph (GC) principle. This simple device (Fig.1a) has been reworked in the last 20 years, creating a new family of portable and fast chromatographs (Fig.1b).

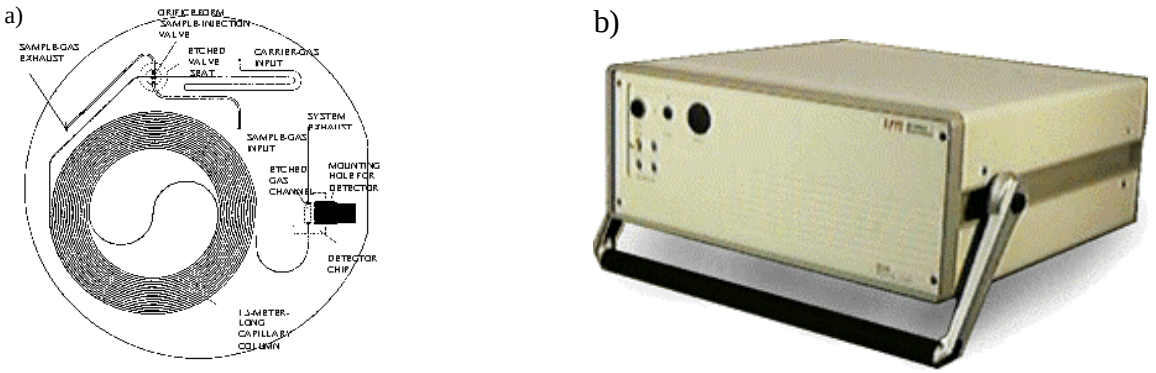

Fig.1: a) The first integrated gas chromatograph made on 2“ silicon substrate [1], b) Portable chromatograph GC MTI Quad 400; dimensions 19x52.5x52.5 cm, weight 20.4 kg, manufactured currently by Hewlett-Packard.

The main aim of the miniaturisation at the first stage of the work was both reduction of analysis time as well as the amount of reagents necessary for the analysis. In 1995/96 a series of portable gas chromatographs, manufactured by MTI (Microsensor Technology Inc.) and based on the solution of 1979 was introduced onto the market. Miniaturisation of

chromatographs enables innovative applications, for example for analysis of astronomical objects in laboratories and on the Earth orbit (the Columbia space shuttle was equipped with very fast micro GC MTI Quad Analyser for the needs of Space Lab). Linking of GC MTI with a microcomputer permitted the hardcopy of analysis results and data transmission to the Earth.

2. Experiment

Our investigation was carried out with application of MEMS technology to fabricate all-parts-micromachined glass-silicon multi-chip gas chromatograph (Fig.2) [2-7].

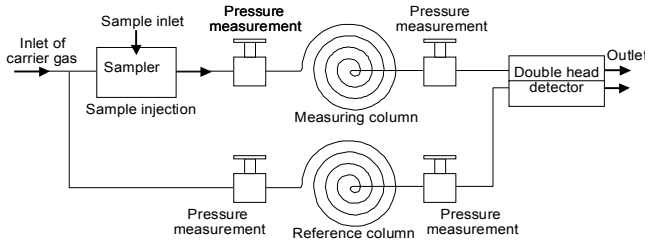

Fig. 2: Schematic constriction of integrated gas chromatograph.

The first step was to develop basic parts of this system:

- silicon capillary column
- dosage microvalve,
- integrated catharometric detector for microflow analysis

Fabrication of silicon integrated column, dosage microwalve and catharometric detector permitted realisation of submicrominiature analyser of gas atmosphere pollution, for mining control and rescue service.

3. Integrated Analysing Column

The basic part of each standard chromatograph (even in GC MTI Quad analyser separation column of Restek MTX® [8] was used) is a chromatography column fabricated by drawing method - similar to the methods applied for fabrication of optical waveguide. Such fabrication method is not capable of distinct reduction of inner diameter of the capillary, however, it is possible to produce the capillaries with considerable length. Poor mechanical resistance and high price of the capillaries forces the development of new methods aiming at manufacture of capillaries with sufficient length and relatively small diameters. Many works on fabrication process of integrated columns both for GC as well as for LC (Liquid Chromatography) have been reported in the literature [9-16].

A complex process of designing, including optimisation of fabrication process in terms of realisation of integrated analysing system for gas microchromatograph has been performed.
Our optimised process consists of:

- Preparation of semi-finished product I, consisting of isotropically etched on ϕ 3“ silicon substrate channels (through oxide mask 1.5 μm thick) with U-profile; with dimension minimal: 35 x 11 μm^2 and maximal: 300 x 150 μm^2, respectively. Geometry control

within limits of +/- 1 µm. The length of the channel, made on 3“ substrate ranges from 12 to 30 m, depending on the geometry of U-profile. After etching, the wafer is covered with 0.2 μm thick oxide layer.

- Preparation of semi-finished product II – Schott Borofloat 33 glass substrate 2 mm thick, with drilled holes and assembled glass and silicon tubing system.
- Assembling of semi-finished products I and II by anodic bonding method.
- Glass wafer with tubing system made by multi-layer anodic bonding process.

A series of columns, compatible with IC processes has been obtained. The length of the columns depends on assumed channel depth. For the columns with 35 μm x 11 μm, channel width and depth following from the applied technological processes, the length of capillary does not exceed 30 m. The silicon GC column and its cross-section is shown in Fig.3.

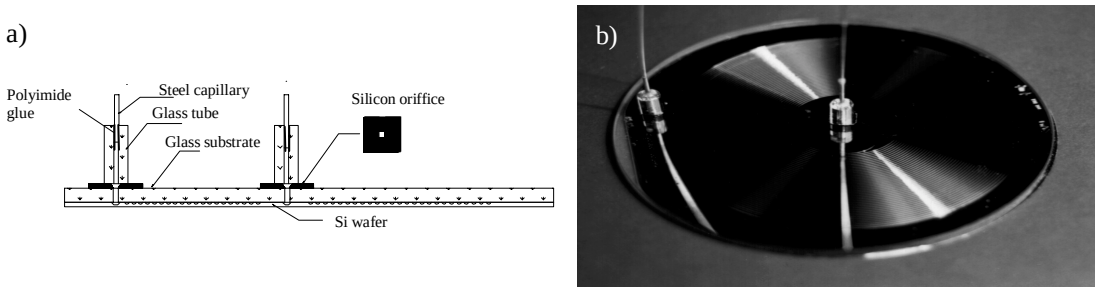

Fig. 3: The silicon GC column a) cross-section, b) natural view.

Application of a special package with connecting ferrules makes the column compatible with tubing systems commonly used in chromatography. Additional case ensures complete resistance of the column to mechanical damages which occurs during typical working conditions. Integrated chromatographic columns, just like the standard ones, demand additional activation process. Activation of the columns consists in covering of inner column walls with a stationary layer. Columns were activated by squalan in standardly used activation process and tested. Our integrated column was used in the Hewlett Packard 5890 II chromatograph, replacing the standard one. The chromatograph was equipped in ionisation-flame detector. The analysis of a mixture of aliphatic hydrocarbons has been performed (n-pentane, n-hexane, n-octane, n-decane). In the following experiment, separation of aromatic hydrocarbons (benzene, toluene ethylobenzene, cumene, sek-buthylobenzene, n-penthylobenzene and naphtalene) has been carried out (Fig.4).

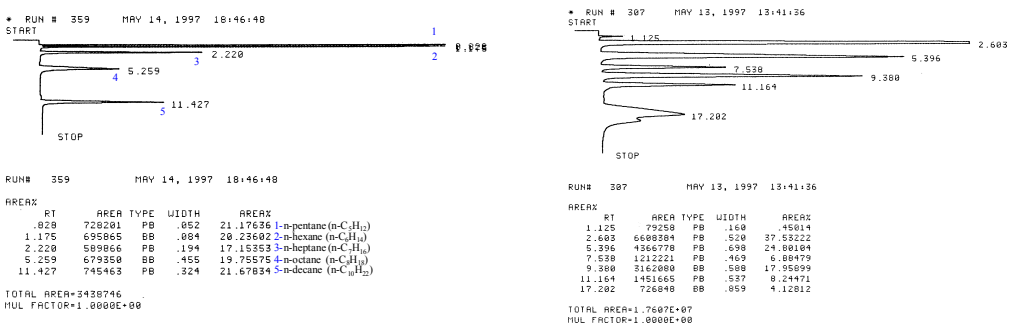

Fig. 4: Chromatograms of separated (a) aromatic, (b) aliphatic hydrocarbons.

4. Silicon Injection Valve

Besides the separation column, a complete chromatograph consists of a dosage system (containers, valves, pumps) and the system for analysis The components take part in analysis process and therefore their technical and operational parameters are very important from the point of view of the quality of obtained results. Miniaturisation and integration of mentioned components is a way of increasing the quality of the gas chromatography system [9,17].

Integrated injection system of gas and their mixtures allowing control and adjustment of microvolumes in capillary flow system consists of three basic components: carrier gas system, sampling valve system, thermoconductive flow sensor and the electronic control system. The scheme of proposed injection system is shown in Fig.5a [18].

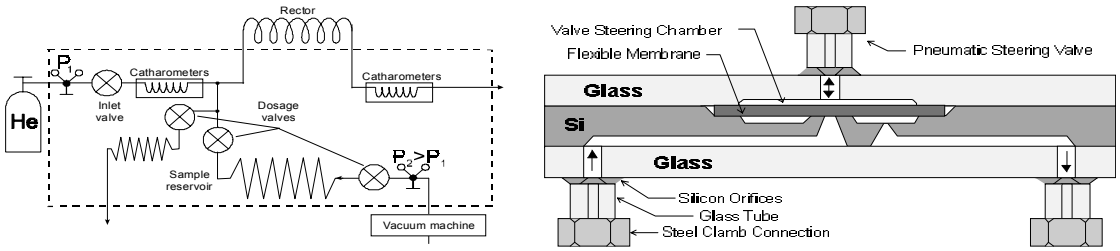

Fig. 5: a) Schematic drawing of gas injection system, b) Cross-section of the sampling valve.

The microvalve was composed of silicon, two glass wafers suitable for anodic bonding process, thin Teflon foil and 3 glass pipes (Fig.5b). Inlet and outlet of the valve, supplying channels and the area for fitting of the Teflon membrane were micromachined in isotropic and anisotropic wet etching process [18,20]. The bottom glass wafer seals the supplying channels and possesses an inlet and outlet holes. At the holes, glass pipes, acting as supplying system, are attached by multi-layer anodic bonding method. All terminals are equipped with steel clamps, enabling connection of additional operating and measuring systems.

The valve is controlled pneumatically with the pressure applied directly into the control chamber. When the pressure inside the control chamber is higher than the gas pressure at the valve inlet, the elastic membrane seals the lever and closes the valve. When the pressure inside the chamber is lower or when reverse pressure is applied, the membrane rises and opens the way for gas flux, causing its flow.

The complete design cycle of fabrication of valve prototype structure has been performed. A micromechanical, totally integrated valve was obtained. Construction details and final structure is show in Fig.6.

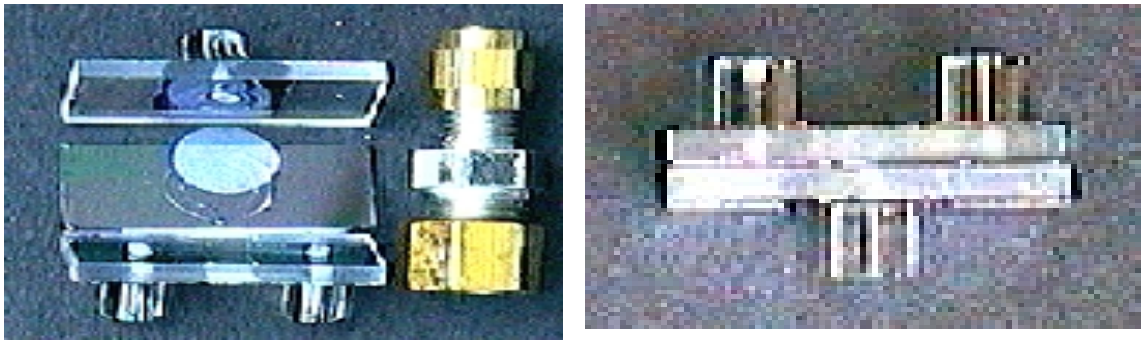

Fig. 6: Silicon micromechanical valve with Teflon sealing membrane; a) construction details, b) final structure.

5. Catharometric Detector

The sensor of flow rate and mass with the dead volume of several microlitres and resolution of several p.p.m. is the basic component of analysing and sampling system for the chromatograph. High demands concerning the sensor performance (sensitivity, resistance to poisoning, fast response) mean that the level of complexity of the fabrication process of the sensor is very high. Therefore, the process of the sensor realisation is one of the most difficult steps in integrated gas microchromatograph design [21, 22, 23, 24].

The structure of the sensor with dimensions 5×5 mm^2 is made of (100) oriented silicon wafer and consists of two parallel flow channels with the length of 5 mm. The channels are connected with two parallel capillary columns. The width, length and depth of the channels in the measuring range are 800 μm, 1200 μm and 250 μm, respectively. From the back side of the substrate via holes positioning Pt heater and thermo-sensor were etched. Inside each channel, two similar coils (ϕ = 300 μm) of thin platinum wire (ϕ = 15 μm, 800 to 1200 μm long) are inserted. The channels are sealed with a glass wafer attached in anodic bonding process. In the glass cover deep grooves are sewed mechanically. This grooves, aligned to previously described channels etched in silicon are used to positioning capillary connection of the sensor to the test gas lines. Change in resistance of the thermoresistors depends on the gas flow rate and is monitored with an electronic control system. The sensor appearance has been shown in the figure 7.

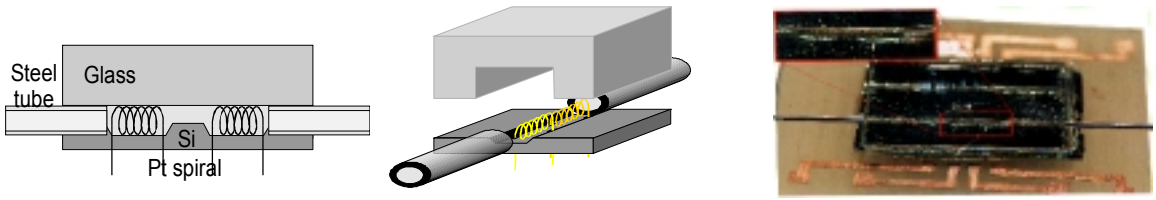

Fig. 7: a, b) The catharometer expanded view and cross-section, c) the die

The catharometer was tested in a model-scale portable gas chromatograph by EMAG (The Centre of Mining Electrification and Automation)). Good sensitivity versus gas type and flow rate was obtained (Fig.8).

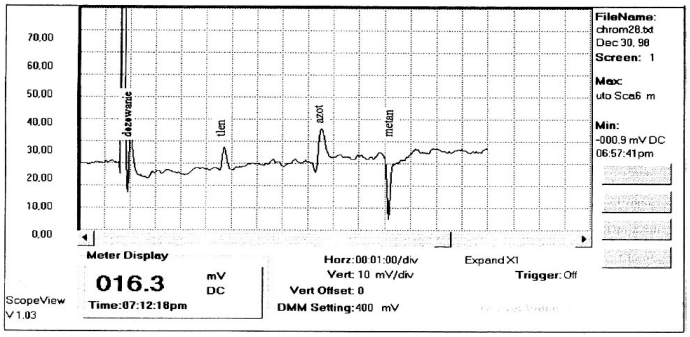

Fig. 8: Chromatogram of the standard atmosphere of deep coal-mine.

6. The Multi-Chip, Integrated Gas Chromatograph

We have obtained main parts of gas chromatograph. All parts were integrated to the form of hybridised 100×100×30 mm^3 Multi-Chip-Module (Fig.9).

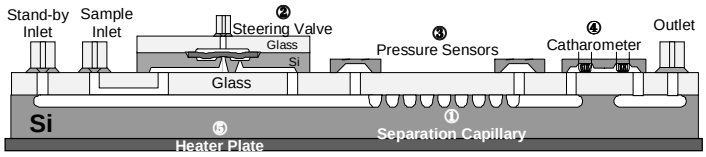

Fig. 9: Cross-section of MCM hybridised gas chromatograph.

The module is equipped in:

- glass-silicon separation integrated column - ▶ ,
- open-closed valves - ▶ ,
- two pressure sensors - ▶ ,
- catharometer and dozing injection system - ▶ ,
- ceramic thick film heater and stabiliser of the temperature - ▶ .

7. Summary

A new concept of integrated gas chromatograph for fast air testing has been proposed. All main parts of the device have been obtained by use of MEMS-like fabrication process.
A silicon-glass capillary gas chromatographic column integrated on to 3“ wafer has been described. Good separation of hydrocarbon was obtained. The new dozing injection glass-silicon-glass valve with floating TEFLON® of Du Pont thin membrane, pneumatically operated has been proposed.

The glass-silicon thermoelectric catharometer with miniature Pt ϕ = 300 μm spirals assembled in micromachined silicon substrate prior to anodic bonding process was developed and tested. Chromatographic tests of artificial deep-mine atmosphere were done. Good chromatographic profiles were obtained. A multi-chip, multi-layer hybridised module 100×100×30 mm^3 of chromatograph was built. Thick-film heater allowed to obtain stabilised ±1 ^oC in the range +40÷+110 ^oC temperature of the module. A capability of microengineering and MEMS-like methods of fabrication toward total integrated of gas chromatograph has been shown. In future projects an optimisation of the design will be ensured.

8. Closing Remarks

The presented results were obtained in the Institute of Microsystems Technology as the results of scientific research at bachelor and master degree level and continues as part of the authors doctoral studies. The Work is strongly connected with industrial application, and is part of a wider research programme financed by State Committee for Scientific Research (KBN) in the period 1995-1998 grants No PBZ 2705, 9T12A03710, 9T12A04613. The research was co-ordinated by scientific mentor Jan Dziuban PhD from our Institute, and by J. Mróz PhD from EMAG Katowice.

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References

1. Terry SC (1975): A gas chromatographic air analyser fabricated on silicon wafer using integrated circuit technology. PhD. Dissertation Stanford University.
2. Dziuban J, Górecka-Drzazga A, Nieradko Ł, Mróz J (1997): Micromachined silicon microcolumns for FIA chromatography with anodic bonded glass inlets and outlets. Chemical and Biological Sensors and Analytical Electrochemical Methods. 192nd Meeting of The Electrochemical Society, Inc. and the 48th Annual Meeting of the International Society of Electrochemistry Paris, France August 31 - September 5, pp. 946-953.
3. Dziuban J, Górecka-Drzazga A, Nieradko Ł, Mróz J (1997): IC process compatible technology of silicon integrated capillary column fabrication. EUROSENSORS XI, Warsaw 21-24 September pp1291-1295.
4. Dziuban J, Górecka-Drzazga A, Nieradko Ł, Mróz J (1996): Silicon Microcolumn for FIA Chromatography. Proceedings of the 2nd Int. Symposium on Miniaturised Total Analysis Systems. μTAS 96,pp.203-205, Basel; 19-22 Nov. 1996, Analytical Methods & Instrumentation, Special Issue μTAS'96.
5. Nieradko Ł, Dziuban J, Górecka-Drzazga A, Mróz J (1997): Silicon microcapillaries for microchromatography (in Polish). ELTE'97 tom 2 736-739, May ISSN 1427-3357.
6. Dziuban J, Górecka-Drzazga A, Nieradko Ł, Mróz J (1997): Silicon integrated capillary for μTAS MST-News no.1(5) pp.8-11, March ISSN 1426-854X.
7. Dziuban J, Górecka-Drzazga A, Nieradko Ł, Mróz J (1997): Capillary microsystems for μTAS (in Polish). Elektronizacja nr 7-8 pp. 7-8, ISSN 0138-0826.
8. Catalogue RESTEK "Chromatography product" 1998.
9. Terry SC et al. (1978): A gas chromatographic air analyser fabricated on silicon wafer. IEEE Trans. El. Dev, ED26; No.2 pp. 1880-1886.

10. Manz A et al.(1994) μTAS: Miniaturised total chemical analysis systems. Proceedings of the μTAS Workshop, MESE Research Institute. 21-22 Nov. pp.: 5-23.
11. Manz A, Graber N, Widmer H M (1991): μTAS - A novel concept for chemical sensors. Sensors and Actuators; B1-1990-pp. 244-248.
12. Manz A et al. (1991): Micromachining of monocrystalline silicon and glass for chemical analysis systems; A look into next century's technology or just a fashionable eraze ? Tren. Anal. Chemistry, 10 pp. 144-148.
13. Effenhauser CS et al. (1993): Glass chip for high speed capillary electrophoresis separation with submicrometr plate heights. Anal. Chem. 65 pp. 2637.
14. Harrison DJ et al. (1994): Integration of analytical systems incorporating chemical reactions and electrophoretic separation. Proceedings of the μTAS Workshop, MESE Research Institute. 21-22 Nov. pp.: 105-115.
15. The 2nd Int. symposium on miniaturised total analysis systems. μTAS 96, Basel; 19-22 Nov. 1996, Lectures of Prof. Prof. Manz, Harrison, Ramsey, Widmer.
16. Catalogue MTI Analytical Instruments, MTI's P200 Gas Chromatograph 1995/1996, Microsensors Technology, Inc. 41762 Christy Street Fremont, CA 94538, USA.
17. Małecki K, Dziuban J, Górecka-Drzazga A (1997): A silicon valve-less pump IC compatible technology. MST News Poland 3/97.
18. Dziuban J, Małecki K, Górecka-Drzazga A, Nieradko Ł: "Design, construction and operation principles of integrated sample system" unpublished.
19. Lammering TSJ et al. (1993): Micro-liquid flow sensor. Sensors and Actuators A, 37-38, 45-50.
20. Dziuban J, Małecki K, Górecka-Drzazga A, Nieradko Ł: An integration of gas microchromatograph components.
21. Mayer F, Paul O, Baltes H (1995): Influence of design geometry and packaging on the response of thermal CMOS flow sensor. The 8th International Conference on Solid-State Sensors and Actuators, EUROSENSORS IX Stockholm, Sweden, June 25-29, 528-531.
22. Moser D, Baltes H (1993): A high sensity CMOS gas flow sensor on a thin dielectric membrane" Sensors and Actuators A, 37-38.
23. Qiu L, Obermayer E, Schubert A (1995): A microsensor with integrated heat sink and flow guide for gas flow sensing application. The 8th International Conference on Solid-State Sensors and Actuators, EUROSENSORS IX Stockholm, Sweden, June 25-29, 520-523.
24. Accorst A (1991): A new microsensor for enviroment measurments" " Sensors and Actuators B,4), 359-543.