MICRO AND NANOTECHNOLOGIES FOR FOOD SAFETY APPLICATIONS

Carles Cané[1], Peter Ivanov[1], Fernando Blanco[2], Isabel Gràcia[2], Luis Fonseca[2], Neus Sabaté[2], Eduard Figueras[2], Joaqiun Santander[2]

[1]Centre Nacional de Microelectrònica. (CNM-IMB-CSIC), Campus UAB E-08193 Bellaterra, SPAIN, Tel +34 93 594 77 00, e-mail: carles.cane@cnm.es

[2] Departament d'Enginyeria Electrònica, Elèctrica i Automàtica, Universitat Rovira i Virgili Av. Països Catalans, 26 Campus Sescelades, 43007 Tarragona SPAIN Tel.: +34 977 558 764,

Microsystems will play an important role in the agro-food field as many different safety and quality assurance procedures may benefit from the inherent advantages of small, fast and reliable devices. An example is proposed for the detection of gases of interest in the control of fruit with a micro-system that combines optical and semiconductor gas sensors. A simple process step is also introduced that allows improving the performances of such devices.

Keywords: micro-systems, μ-hotplate gas sensors, optical sensors, preconcentrators

1. INTRODUCTION

Food safety and quality assurance play an important role for the increase of the confidence of consumers and agro-food industry is quite concerned in finding out new test solutions for the different stages of the complete food chain. Nowadays main tests are performed with laboratory based systems, which are well accepted due to the good accuracy, but lack from flexibility and are usually very expensive and time consuming. In this way, tests are performed randomly in different food samples, which mean that they are not universal. Thus, there is a real interest in looking for new solutions based on novel technologies that may help on the massive test of samples. Immuno-sensors, DNA chips, electrochemical devices, Preconcentrators, portable multi-sensing systems, optical and magneto based assays, etc…, may be of high importance in the future if they benefit from the introduction of micro-system solutions, as they will bring well appreciated advantages on miniaturization, fast response, cost reduction, electronics reading. For the specific application of micro-systems to the agro-food field, these characteristics will lead to portable instrumentation for massive and ubiquitous field and at-line tests. In this way they will be very adequate for food screening applications in a HACCP (Hazard Analysis Critical Control Point), because of a reduction of time for tests and of the reagents required, and because of the improvement of the capabilities of communication that enables setting an smart information loop useful for the decision taking and risk management at all stages of the food chain.

As an example, a micro-system intended for the quality detection of climacteric fruit during storage is proposed in this work. Usually, quality of fruit is associated to the ripeness degree that is controlled during long storage periods in order to reach the market at the proper time. Thus, during storage fruit is maintained at low temperature and under low oxygen environment. Ethylene is emitted by fruit during ripeness and hence, it is of interest to determine its concentration in the chamber. In addition, an important problem during storage is the potential leakage of ammonia coming from the refrigeration system. In conclusion, a micro-system that can help on the parallel determination of both gases is of interest. Optical and semiconductor gas sensors may be used for the purpose, but up to now no commercial devices are available for such application. Moreover, both gases use to interfere the other one when using single gas sensors and for this reason the proposed solution is a combination of both semiconductor and optical gas sensors, as shown in Figure 1, in order to improve the selectivity of the system. The optical part is an infrared device composed of an emitter, an absorption chamber, and an infrared detector. On the other hand, the semiconductor gas sensor array is composed of four thin membrane based micromachined devices, that properly packaged is also placed in contact with the gas flowing through the chamber.

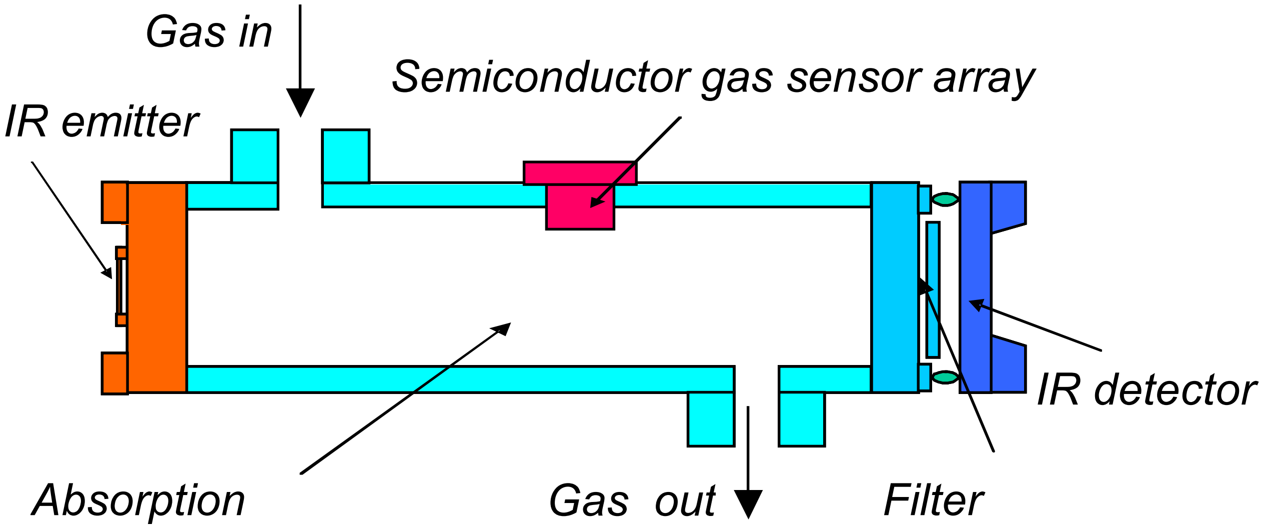
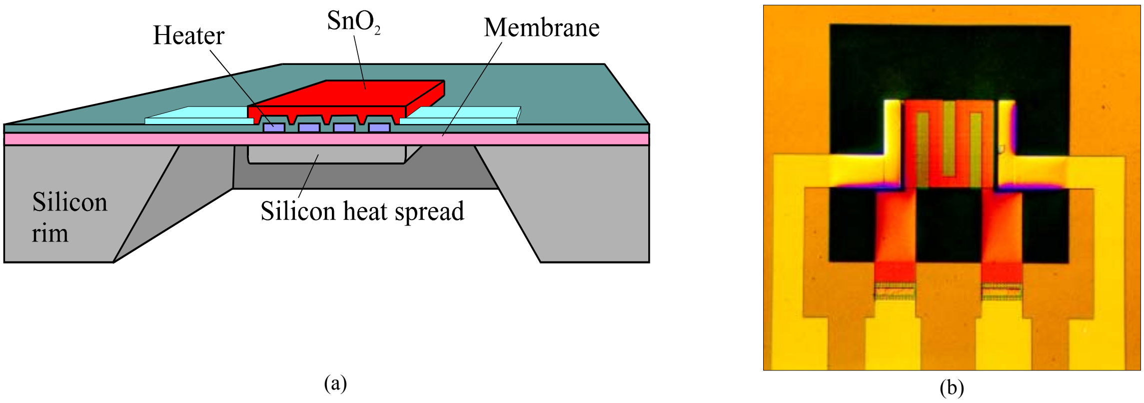


Figure 1. Schematic view of the proposed micro-system.

The present paper describes the main fabrication steps required for the obtaining of micromachined structures for the semiconductor gas sensor substrates and for the infrared detector, as the two basic parts of the system. Special interest will be put in a deep diffusion process step that will show their applicability for improving the performances of such devices. This paper does not cover the implementation of an micro IR emitter, as commercial devices may be integrated.

2. SUBSTRATES FOR SEMICONDUCTOR GAS SENSORS

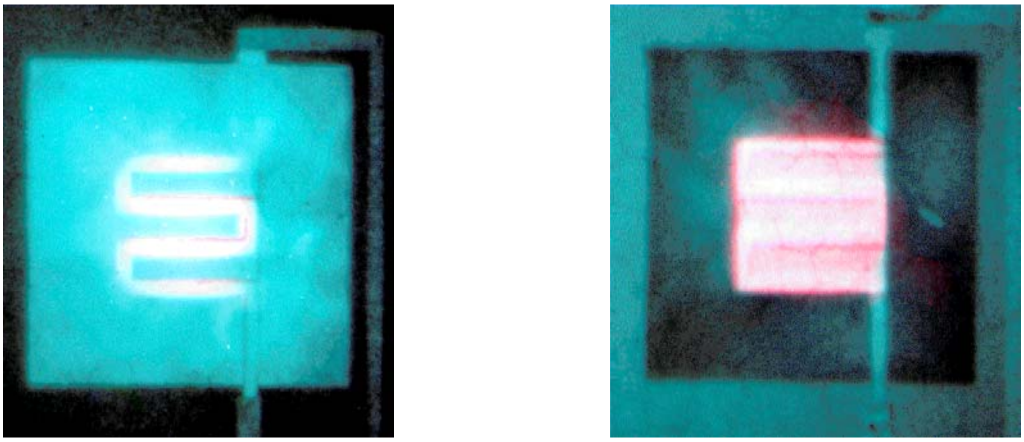
Thin film semiconductor gas sensors are usually fabricated on thermally isolated silicon substrates in order to show low power consumption and fast response. Figure 2 shows a schematic cross section and a top photograph of one of these sensors.



(a) (b)

Figure 2. (a) schematic cross section and (b) top view photograph of a silicon micromachined semiconductor gas sensor with an integrated silicon heat spread.

The sensor basically consists of a gas sensitive material placed over a dielectric membrane which also incorporates a heater in order to set the operation temperature for the materials. The proposed device also integrates a silicon plug or heat spread below the sensitive material that improves the specifications of the sensor in terms of homogeneity of the operating temperature (thus improving selectivity) and of the mechanical robustness. In Figure 3 thermal emission images obtained with a Scanning Emission Microscope of membranes of 1 mm^2 with and without a plug of $500x500\mu m^2$ are compared. It is shown that thermal homogeneity of the active area on which the heater is placed improves independently on its layout.



(a) (b)

Figure 3. Scanning Emission Photograph of the temperature distribution achieved by a meander heater over a silicon nitride membrane a) without and b) with a silicon heat spread below the active area.

The device fabrication process starts with a masked high dose boron diffusion to obtain the silicon plug below the active area as it will be detailed in a next paragraph. Then a 30 nm LPCVD Si_3N_4 that acts as membrane material is deposited and it is implanted with boron ions at 1e15 cm^{-2} and 100 KeV in order to reduce the inherent intrinsic stress. Over the nitride, a layer of 480 nm of polysilicon is deposited and n-type doped with POCl3. A layer of deposited SiO_2 acts as electrical isolator between the heater and the sensitive layer. Cr/Pt (250 nm) electrodes patterned with lift-off are defined. Then, thin or thick semiconductor oxide materials are deposited over the active area. Specific materials with improved sensitivities to the target gases of the application are currently being studied. The device is completed with the back side anisotropic etching with KOH (40%wt.) at 75ºC. Etch is automatically stopped at the dielectric membrane and at the edge of the highly boron doped silicon plug.

3. STRUCTURES FOR IR RECEIVERS.

Least cost uncooled infrared micromachined receivers are usually based on microbolometers or thermocouples that measure the temperature variation due to the IR signal that reaches the receiver after the adsorption of the gas under test in a chamber. For the proposed microsystem, a 2-chip implementation based on an array of themopiles and an array of unspecific passive filters is proposed, as shown in Figure 4.

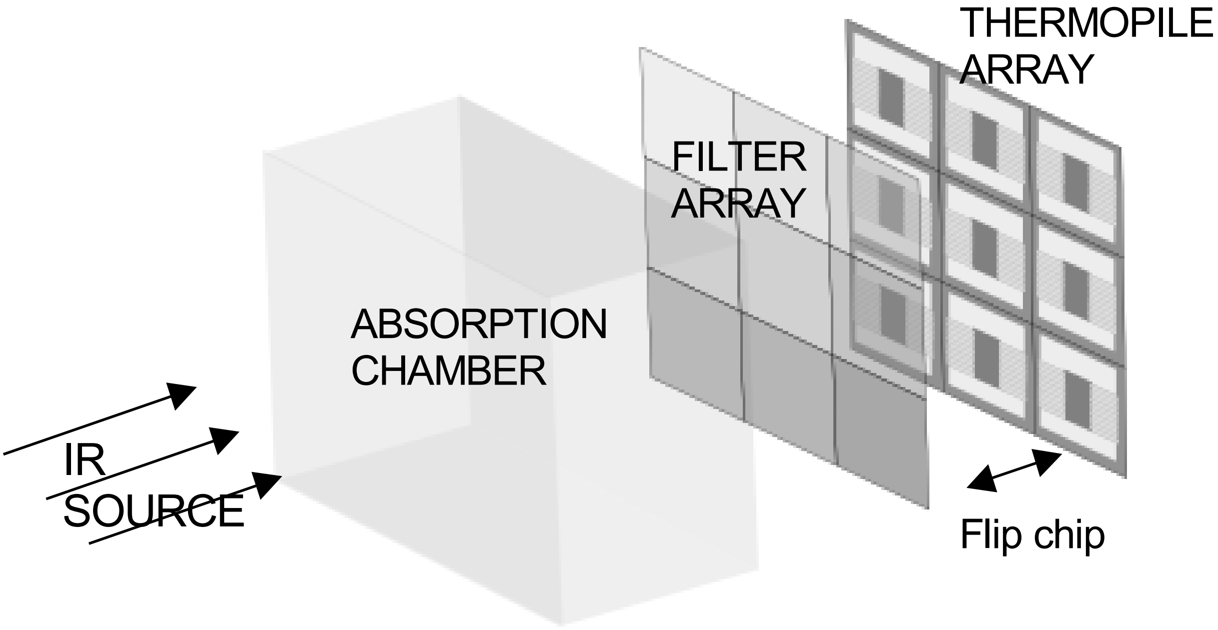
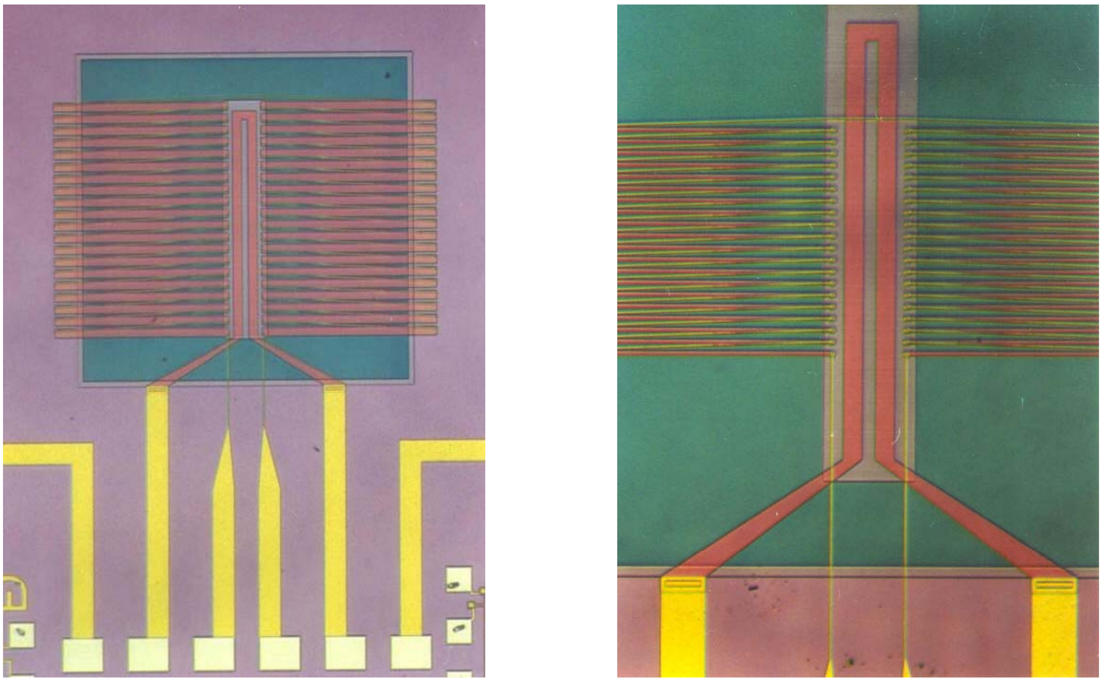


Figure 4. Gas detection system architecture.

The absorption chamber containing the gases to be detected is illuminated by an infrared source, then the radiation goes through the array of filters that selects a different part of the spectrum for each sensor and the final output is a voltage pattern that has to be processed. The filter array is built over a silicon substrate alternating thin films of different index and acts like a Fabry-Perot structure with multiple transitions peaks in the IR region of interest. On the other hand, the micromachined sensor array consists of nine thin and freestanding nitride membranes with isolated thermopiles. Each thermopile consists of a set thermocouples made of n-doped polysilicon and aluminum. The hot contacts of the thermocouples are formed on the thermally insulating membrane and the cold contacts are placed on the silicon rim of the structure, which acts as a heat sink. The absorber, which converts the IR radiation into thermal energy, defines the sensitive area. Each individual thermopile sensor structure is sketched in Figure 5.

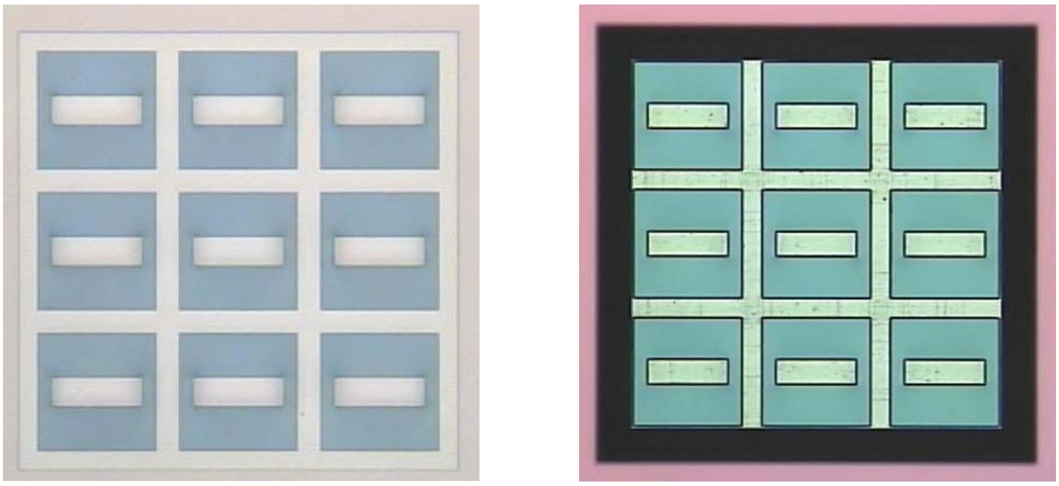


a) b)

Figure 5. (a) General view of a micromachined thermopile, and (b) detail. The nitride membrane, the silicon absorber, the self-test heater and the polysilicon and aluminum thermocouples can be seen.

The thermopile fabrication technology has been made fully compatible with the previous technology established for the fabrication of micro-hotplates for semiconductor gas sensors. The high thermal resistance membrane, that in the later case isolated the high temperature region from the silicon rim in order to lower the power consumption, assures in the former case the temperature isolation between junctions allowing a temperature difference to develop when IR radiation reaches the absorber layer. The under-platform silicon plug that kept the temperature uniform in the gas sensor, acts now in the thermopile as a unique absorber taking advantage of the infrared absorption properties of heavily doped silicon. With such implementation it has been measured the transmittance of the silicon plug being nearly zero, which means that it is a good absorber for a infrared sensor, without any additional material.

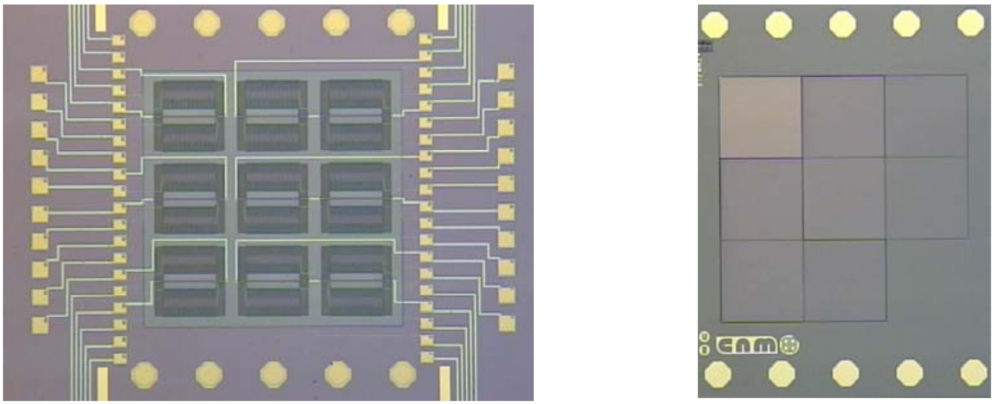
As a new improvement of the device, the deep boron diffusion process is not only used for defining the IR absorption regions, but also for allowing an array design for which all thermopiles are fabricated over the same isolating membrane. To ensure the existence of hot and cold junctions for each detector we define on the insulating membrane absorbers and ribs, 6µm deep, by boron heavy doping. The ribs, which are 120µm wide, crisscross the membrane contacting the silicon bulk and thus acting as a heat sink. Absorbers are located in the center of each individual pseudo-membrane defined by the ribs intersection, as shown in Figure 6, from front and back photographs. Incident radiation heats up the absorber creating a temperature difference that is measured by the thermocouples that are placed between the absorber and the ribs.



(a) (b)

Figure 6. (a) Front and (b) back photograph of the 3x3 array of silicon plugs and ribs in a single membrane for the thermopile array implementation.

The single detector size is of 620x620 μm^2 for the 3x3 array. Devices have been micro-machined with a high yield, proving that the mechanical stability of the 4 mm^2 membrane is improved by the structural role of the silicon ribs. A fabricated 3x3 thermopile array can be seen in Figure 7, altogether with the filter array.



(a) (b)

Figure 7. Photograph of (a) the complete 3x3 thermopile array and (b) of the 3x3 unspecific passive filter array.

Both dies have been attached using flip-chip techniques into a single detector module.

4. THE PROCESS FOR DEEP BORON DIFFUSION

In the former paragraphs it has been shown that the introduction of the deep boron diffusion process has helped on the implementation of very interesting structures for both semiconductor gas sensor substrates and thermopile arrays. Now the process is described. By thermal simulation it was determined that a depth of 5 to 10 microns is enough for achieving a good thermal conduction and temperature homogeneity, and the temperature and times for achieving such results were also obtained by technological simulation. The process is performed in two steps. First a pre-deposition of boron is made by using BN-1250 solid source wafers at 1240ºC during

60 min., followed by a drive-in process under oxygen ambient during 60 min at 1150ºC. In Figure 8 the profile obtained by Spreading Resistance and the etch rate at 75ºC with KOH are plotted. It is shown that boron bulk concentrations in the range of 1e20 at/cm^3 are achieved for a depth of around 10 microns.

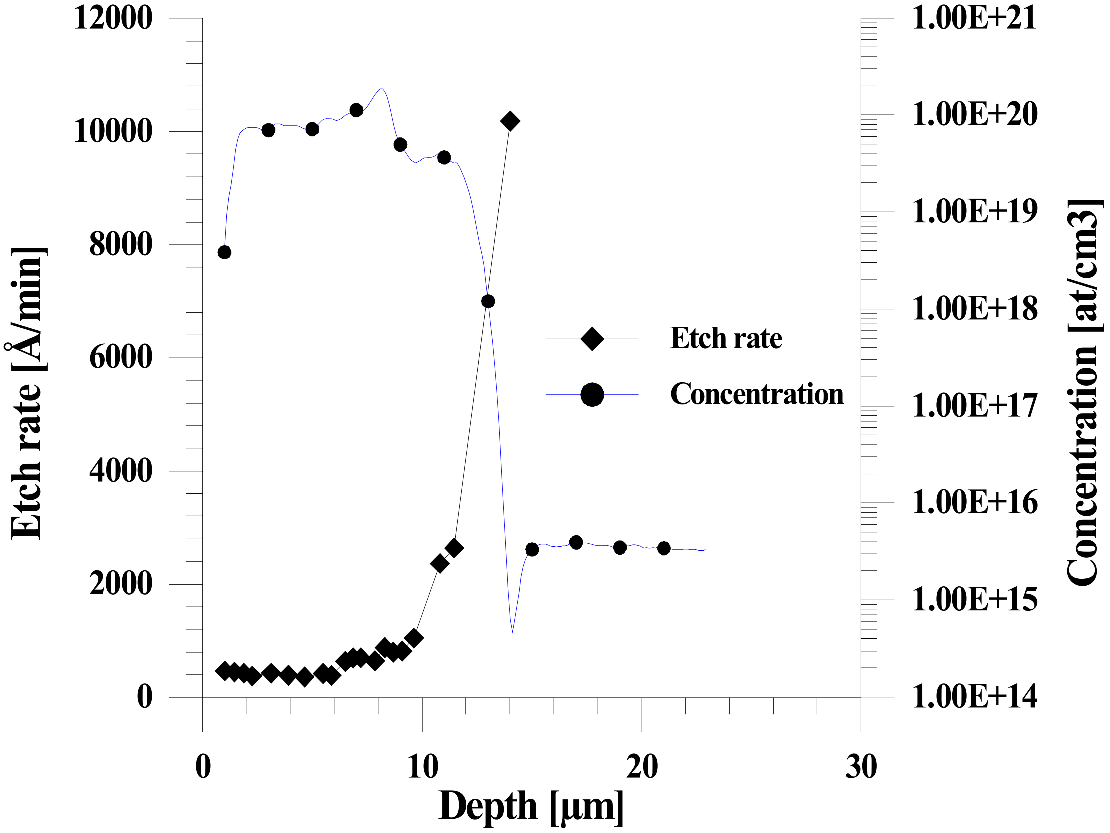


Figure 8. Boron concentration profile and etch rate of silicon in KOH obtained with the proposed deep boron diffusion process.

For such concentrations, etch rates 25 times lower than the ones achieved with standard doped silicon are obtained. This means that the backside etch process can be considered as an automatic etch stop process, making the fabrication of the structures very simple.

5. PREONCENTRATOR DEVICES

Miniaturized gas chromatography systems are of particular interest in applications, where portability, reliability and low-cost are compulsory. Miniaturization leads to an improvement of heating rates, power consumption and allows integration in portable devices. A specific application of such portable devices concerns the on-field monitoring of parameters related to the hazard compounds and environmental contamination. Sometimes the concentration of the target gas is too small and below the detection levels of the existing gas sensors.

The preconcentrator consists of an absorbent material placed on a heating support. When a preconcentrator is used, the gas mixture to be analyzed flows through it and is accumulated during a certain time. Then the mixture is desorbed altogether by a temperature pulse and driven to the sensor array. Novelties in this field were the development of a micro fabricated multiple-stage preconcentrator-focuser reported in 2005 by Tian. Another approach consists of micro machined devices consisting of a thin layer of adsorbent film on a heated membrane developed by Sandia National Laboratories.

The first approach to the development of the micro-preconcentrator consists of a spiral-shaped channel, housing the porous adsorbent powder. The proposed structure is extremely versatile and permits to connect various spirals in series in order to increase the operating volume if needed. The temperature pulses are provided by a Platinum heater patterned on the pyrex glass cover. The μ-preconcentrator was fabricated on silicon by means of Deep Reactive Ion Etching (DRIE) and anodic bonding techniques, as follows: (a) p-type Silicon wafers (1 0 0) double side polished, with thickness of 500 μm and resistivity of 4-40 Ω cm have been used as substrate; (b) Resist MaP1275 has been used as mask in the DRIE process that defines the spiral-like column configuration (c) A Pt heater has been defined in a Pyrex substrate by the lift-off technique. (d) Finally, the silicon wafer has been sealed to the Pyrex cover plate by anodic bonding. Figure 9 shows the fabricated structure.

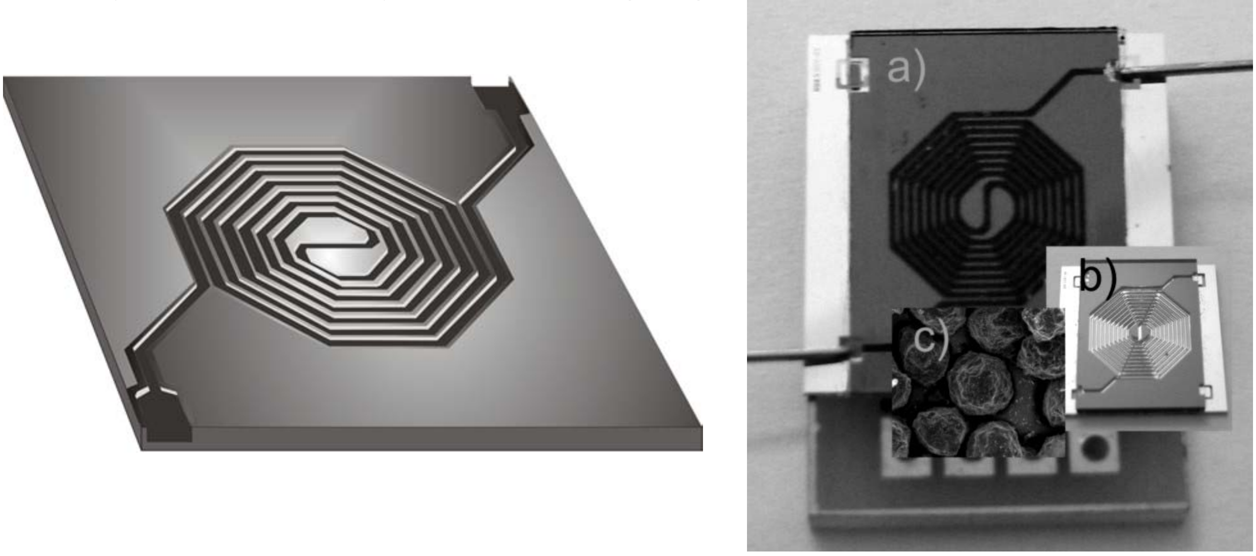


Figure 9. Schematic view of the fabricated structure (left), a) Front view of the spiral shaped μ preconcentrator filled with Carbopack X with the details of inlet/outlet and micro-needles connected. The device dimensions are 10 cm × 300 μm × 300 μm (LxHxW); b) Empty spiral; c) Active material (right).

Another approach consists in a fabrication of micro-preconcentrator unit that consists of a 3D-microheater surrounded by an insulating membrane. The preconcentrator is made up of a grid of suspended silicon bars underneath a polysilicon resistor. The grid was formed by 40μm-wide, 520μm-depth, 3000μm-long silicon bars fabricated by deep reactive ion etching covering a 3x3 mm^2 area. A pyrex die with fluidic interconnections has been glued as a top cover onto each chip. This type of silicon grid structure allows to hold large amount of absorbent materials and provides efficient heat diffusion. The dimensions of the μ-preconcentrator were defined to achieve good thermal isolation and high absorbent content to yield a high gas concentration factor. Thermal characterization of the heater showed a low heat capacity of the structure and therefore, fast response and high power efficiency. Figure 10 shows a schematic top-view of the proposed structure.

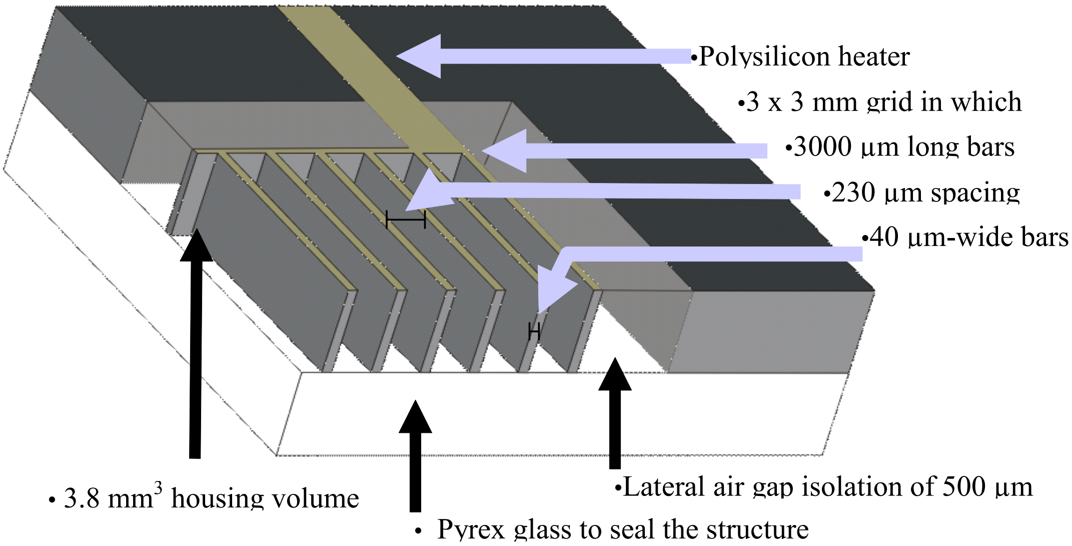


Figure 10. Schematic top-view of the proposed structure.

The silicon grid structure of the µ-preconcentrators was fully loaded with absorbent material. Photograph of the packaged µ-preconcentrator can be seen on Figure 11.

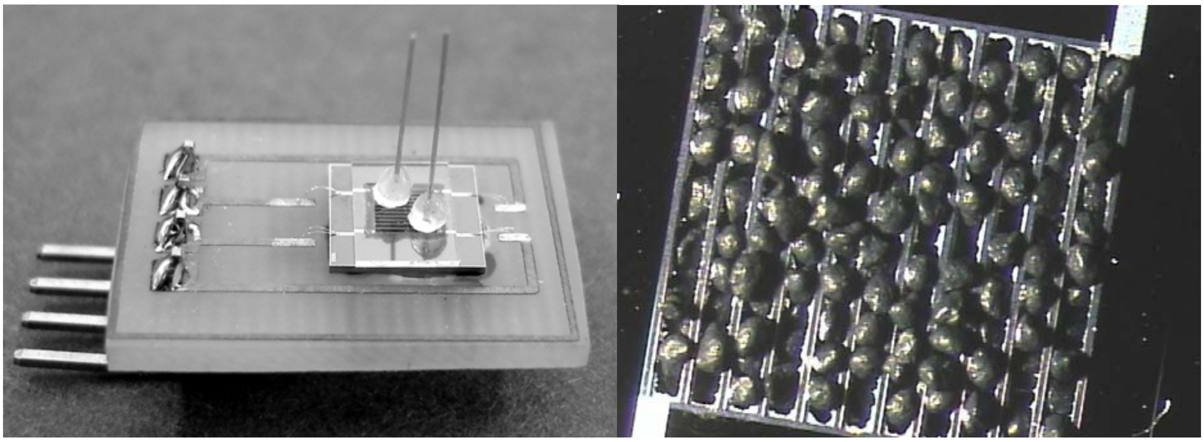


Figure 11. Photograph of the packaged µ-preconcentrator (left); Image of structures filled with absorbent material (right).

6. CONCLUSIONS

A deep boron diffusion technique has been presented as an interesting process step for the improvement of the robustness and of the thermal characteristics of both micromachined substrates for semiconductor gas sensors and for thermocouple arrays working as detectors of an infrared system. A 6 to 10 microns depth boron diffusion has been proved to be a good process to define silicon plugs and ribs that work very well as thermal conductors and infrared absorbers and also improve the mechanical characteristics of thin membrane based micromachined structures. This technological process has been applied to the fabrication of two of the main devices forming part of a complete gas sensing microsystem. On one hand the combination of different kind of sensors is required for improving the selectivity of the system that in any case also requires further signal processing and electronics integration. On the other hand, the incorporation of preconcentrator device that provides concentration factor of up to 500, improves the response of gas the sensors to the ppb range. This will permit the development of portable devices with enhanced effectiveness, capable of almost real-time sub-ppm detection. Combining microhotplate gas sensors with the µ-preconcentrator, a battery-powered device can be developed. This microsystem presented above is intended for the detection of ethylene and ammonia, two gas targets in the food industry when controlling the ripeness process of fruit under long cooling storage stages.

7. ACKNOWLEDGEMENTS

Part of this work has been financially supported by the Spanish Ministry of Education and Science, project: Development of a Gas Chromatography based on Micro and Nano Technology CROMINA (TEC2004-06854-C03-01).