

# Planar Micro Flame Ionization Detector

Winfred. J. Kuipers, Jörg Müller

**Abstract**—Miniaturization of the Flame Ionization Detector (FID) is expected to increase its use, because of reduced oxyhydrogen consumption, which loosens safety precautions and makes portable applications possible. Moreover, in a miniaturized system the minimal required electric field strength is obtained at lower voltages. In contrast to a former micro FID design, the currently presented planar micro FID is designed to prevent environmental air from entering the system and thereby deteriorating the measurement signal. A guard electrode is integrated to by-pass leak currents past the picoammeter. Preliminary measurements show expected FID behavior and a minimal operating voltage of only 50V.

**Index Terms**—Micro flame ionization detector, Miniature oxyhydrogen flame, Mobile gas chromatography, Portable hydrocarbon detection

## I. INTRODUCTION

Flame Ionization Detectors (FIDs) are used in research and industry to quantify organic compounds by first ionizing individual carbon atoms in a high temperature oxyhydrogen flame and then measuring the ion current established by an electric field. In comparison with other analysis systems FIDs have a high sensitivity, a low detection limit and a broad linear measuring range. Moreover, a fast response time makes them suitable for online measurements. In spite of these outstanding characteristics, the use of the FID has decreased over the last decennium. Not because of the availability of more accurate detectors, but because of the high safety precautions enforced by the high fuel gas consumption, which is needed to maintain a stable oxyhydrogen flame. Safety precautions preventing explosions can only be fulfilled in stationary laboratories making the FID incompetent with new generation portable analysis systems.

Miniaturization of the FID seems to be the solution to its problem, as reduced oxyhydrogen consumption loosens safety precautions and makes portable applications possible. Furthermore, in a miniaturized system the minimal required electric field strength is obtained at a lower voltage than in a conventional FID. The minimal voltage of a conventional FID is about 100V, operating voltages range from 200 to 600V [1].

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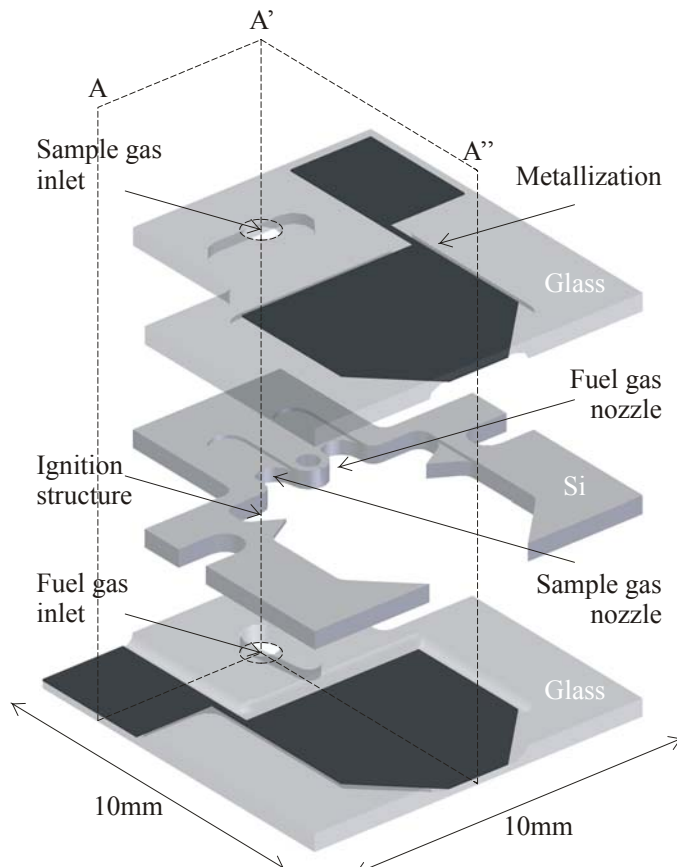


Fig. 1. Exploded view of the planar  $\mu$ FID

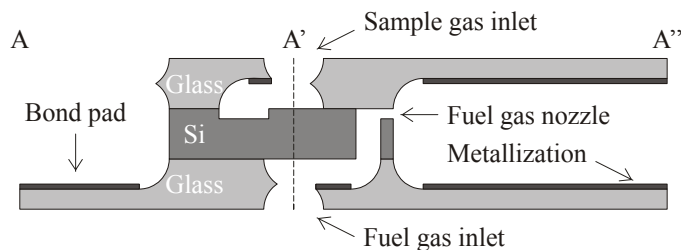


Fig. 2. Cross-sectional view of the planar  $\mu$ FID (The cross-section A-A'-A'' corresponds with Fig. 1.)

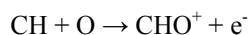
A former micro FID ( $\mu$ FID) design [1]–[3] consists of a glass-silicon-glass sandwich with the flame burning orthogonally to the system in open air. Its performance approaches those of conventional systems, but accuracy and reliability are limited due to external influences on the flame. Other disadvantages of the open burning flame are: - the impossibility of operation in explosive environments, - the need for a glass tube as a flame chamber, being incompatible with microsystems technology, and - heat losses preventing further reduction of the fuel gas consumption. All these problems are tackled by the current planar  $\mu$ FID design, in

which the flame burns in the silicon plane of an almost fully encapsulating glass-silicon-glass sandwich (Figs. 1 and 2).

## II. MEASUREMENT PRINCIPLE

The measurement principle of the FID is based on chemical ionization of organic substances in an oxyhydrogen flame [4]. The ions are accelerated in an electric field, which in conventional FIDs is applied between an annular electrode (anode) surrounding the flame and the fuel gas nozzle (cathode). The concentration of organic compounds within a sample gas results from the ion current density, which can be measured.

When organic compounds are led into a high temperature (2700°C) oxyhydrogen flame, pyrolysis takes place and hydrocarbon radicals are formed. These radicals react with oxygen radicals to a large number of detectable ions:



As a result, the ion current is proportional to the number of carbon atoms present in the sample gas. During oxidation, a large amount of energy is released, which is needed for ionization. As the flame temperature itself is insufficient for ionization, prerequisite for detection is the ability of the compound to form hydrocarbon radicals by pyrolysis. Therefore, FIDs are insensitive to inorganic substances and already oxidized substances like carbon monoxide and carbon dioxide.

## III. DEVICE DESCRIPTION

Important in the design of a  $\mu$ FID is to prevent environmental air from entering the system and thereby reducing its accuracy, which turned out to be the major problem of a former  $\mu$ FID design [1]–[3]. The flame of the planar  $\mu$ FID presented in this paper burns in the silicon plane of an almost fully encapsulating glass-silicon-glass sandwich (Figs. 1 and 2). A small opening remains for the removal of water, which is the combustion product of oxyhydrogen, from the system. If the opening is small enough, it might even be completely closed by liquid water.

The metallized glass surfaces on either side of the flame reflect heat back into the flame, thereby reducing the amount of fuel gas needed to produce enough heat to keep the combustion reaction going. Stable miniature flames are further enabled by symmetrical sample gas supply on both sides of the flame. All contacting edges are rounded in order to prevent cracks, caused by thermal stress between the glass and the silicon. For now, in order to prevent pressure drops over the gas supply lines, orthogonal gas supply over large diameter tubing is preferred over in plane gas supply over small diameter capillaries.

In order to be able to measure ion currents in the nA-range, the system is provided with a guard electrode, in addition to the measurement electrodes as shown in Fig. 3. The guard electrode is positioned on the bottom glass substrate and surrounds the anode.

Leak currents flowing from the silicon substrate (cathode) to the anode are now intercepted by the guard electrode and by-passed past the picoammeter. Only the electrons which are generated in the oxyhydrogen flame are collected by the anode and only the corresponding ion current is measured by the picoammeter.

Leak currents result from both, conductive moist gathering on the flame chamber surfaces during hydrogen combustion and non-zero conductivity of borosilicate glass at elevated temperatures. It is not possible to use non-conductive glass, as the conductivity is needed for anodic bonding during fabrication.

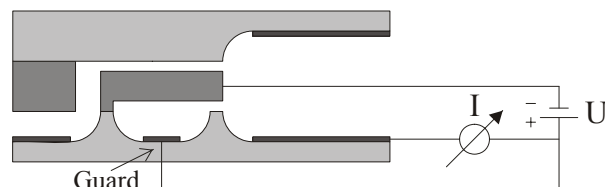


Fig. 3. Cross-sectional view of an electrically connected planar  $\mu$ FID with integrated guard electrode for measuring ion currents in the nA-range

## IV. FABRICATION

Fabrication of the planar  $\mu$ FID with integrated guard electrode starts with patterning gas inlets and flame chamber cavities in both (top and bottom) glass substrates. First, a 200nm poly Si layer is deposited on the glass substrate, which, together with a thick (6,5 $\mu$ m) photoresist (AZ<sup>®</sup>9260) layer, protects the glass substrate from 50% HF wet etching, after the photoresist layer has been patterned by lithography and the poly Si mask has been opened by SF<sub>6</sub> dry etching (Fig. 4a). For orthogonal gas supply, the glass substrates have to be etched through completely. Therefore, the glass substrates (500 $\mu$ m thickness) are etched more than half through (300 $\mu$ m) from both sides. Then the metallization has to be patterned into the flame chamber cavities. As it is difficult to apply photolithography in deep cavities, the metallization is patterned by self-aligned lift-off of the photoresist mask used before for wet etching, after 20nm Cr (adhesion layer) and 80nm Pt have been evaporated on top of it (Fig. 4b). As the metallization on the bottom glass substrate not only serves as a heat reflector, but also as a measurement electrode, this substrate has to be provided with cavities for wiring and contact pads, as well as with a cavity for the guard electrode. Finally, the poly Si is removed completely by SF<sub>6</sub> dry etching (Fig. 4c).

Si substrate processing starts with growing 3 $\mu$ m SiO<sub>2</sub>, which serves as extra protection of the Si from etching. Then, a photoresist (AZ<sup>®</sup>6632) layer of 4.5 $\mu$ m thickness is patterned into flame chambers on the bottom side of the Si substrate by photolithography and the oxide is opened by Advanced Oxide Etching (AOE<sup>®</sup>) [5] subsequently (Fig.4d). Then, the photoresist is stripped and a second, thick (8.5 $\mu$ m) photoresist (AZ<sup>®</sup>6632) layer is patterned into anti-bonding structures to prevent the glass in between the electrode and the guard electrode from bonding with the Si substrate (Fig. 4e). However, the exposed SiO<sub>2</sub> is not removed until the previously exposed Si is anisotropically etched by Advanced

Silicon Etching (ASE<sup>®</sup>) [6] up to a depth of 300 $\mu$ m (Fig. 4f). Then, after the exposed SiO<sub>2</sub> has been removed, the Si is etched another 100 $\mu$ m to obtain anti-bonding structures of 100 $\mu$ m depth (Fig. 4g).

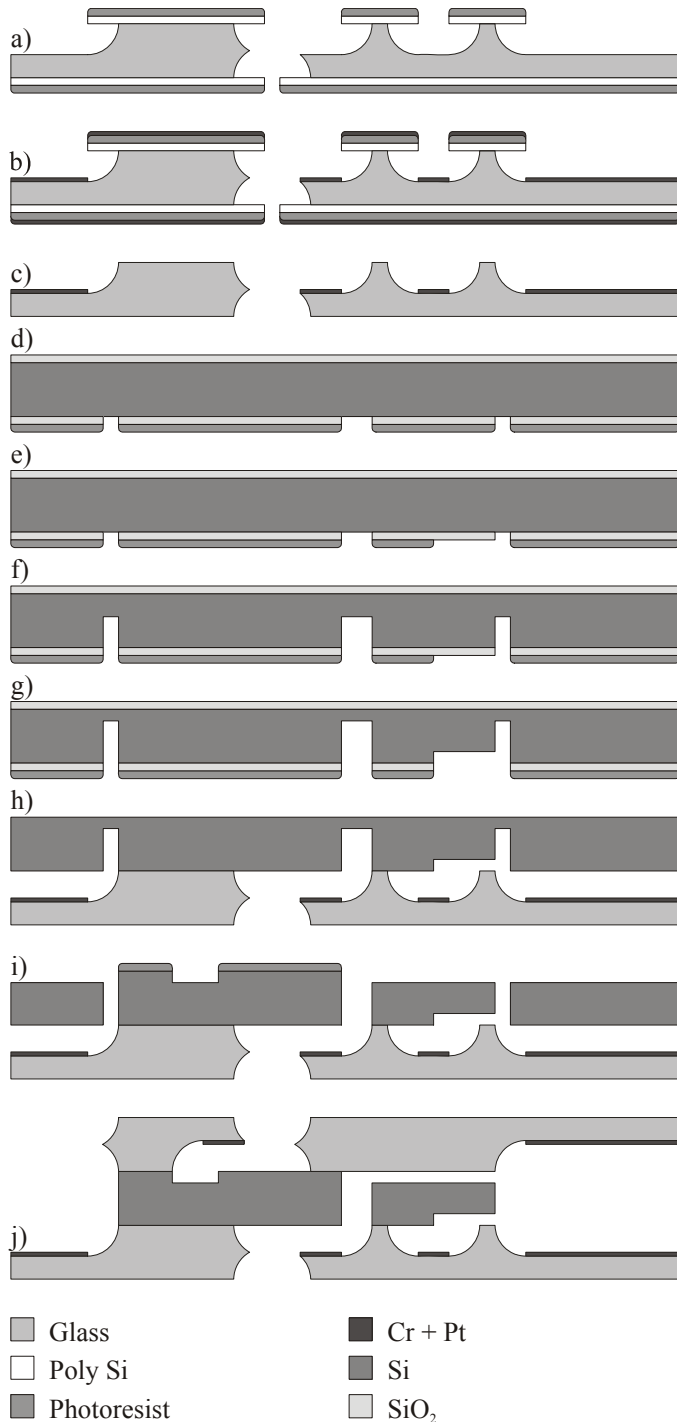


Fig. 4. Fabrication sequence of the planar  $\mu$ FID with integrated guard electrode

To obtain high and homogenous etch speed, the surfaces to be etched are kept small; the flame chamber is not etched away completely, but only a 200 $\mu$ m channel is etched around it. The inner part will be released and removed after the remaining 100 $\mu$ m have been etched from the Si top side later. First, the remaining photoresist is dissolved and the SiO<sub>2</sub> is

removed from the Si substrate by 50% HF, before its bottom side is anodically bonded [7] to the corresponding glass substrate (Fig. 4h). Then, the nozzles are patterned on the Si top side by photolithography (8.5 $\mu$ m thick AZ6632) and structured by ASE (Fig.4i). The flame chambers are etched through during the same process. Finally, also the top glass substrate is anodically bonded to the Si (Fig. 4j).

Fig. 5 shows a single system without integrated guard electrode (according to Figs. 1 and 2) after dicing. As the contact pads of 4 systems are joined together, the metal is cut through during dicing resulting in contact pads, which are easily accessible for soldering.

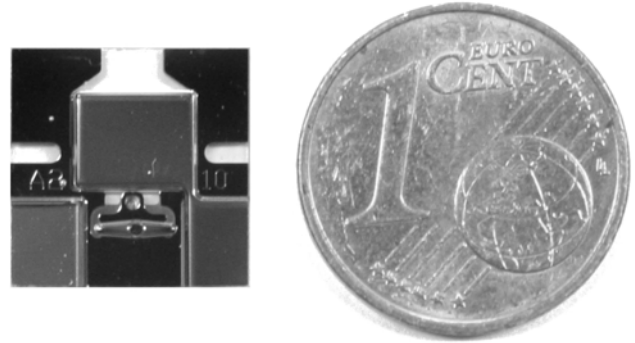


Fig. 5. Planar  $\mu$ FID without integrated guard electrode viewed from the top side

## V. EXPERIMENTAL RESULTS

Measurements with the planar  $\mu$ FID with integrated guard electrode have not been performed yet. Instead, the electrodes of the planar  $\mu$ FID without integrated guard electrode shown in Fig. 5 were mechanically separated to exclude any leak currents during preliminary measurements (setup shown in Fig. 6). As a result, the electrode distance during the measurements was 3mm and not as small as 0.5mm, which it is in the planar  $\mu$ FID with integrated guard electrode.

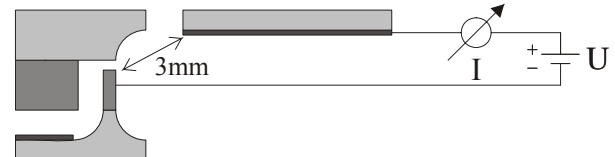


Fig. 6. Measurement setup with mechanically separated electrodes

During all measurements the oxyhydrogen flame was fuelled with 10ml/min hydrogen and its stoichiometric equivalent of 5ml/min oxygen through a nozzle of 35 $\mu$ m width and 100 $\mu$ m depth ( $3.5 \cdot 10^{-9} \text{m}^2$ ), thereby obtaining a calculated outflow velocity of 71m/s. The sample gas consisting of nitrogen with a mixture of different organic compounds adding up to a carbon atom concentration of 2.5% was added to the flame through two nozzles on either side of the flame with a total cross-sectional area of  $1.4 \cdot 10^{-7} \text{m}^2$ . With flows up to 13ml/min sample gas, negligible outflow velocities were obtained. For comparison, 7ml/min pure nitrogen was tested as well.

At 300V and a sample gas flow of 7ml/min 11.1nA was

measured with and 0.5nA was measured without the mixture of organic compounds (2.5% carbon). Without any sample gas at all, the current measured 0.3nA. Fig. 7 shows the voltage versus ion current characteristic, which is in full agreement with the theory [4]. Except for small field strengths, the characteristic shows complete polarity symmetry. The ion current saturates above 50V (below -50V), where the ion current is directly proportional to the amount of carbon atoms present in the sample gas.

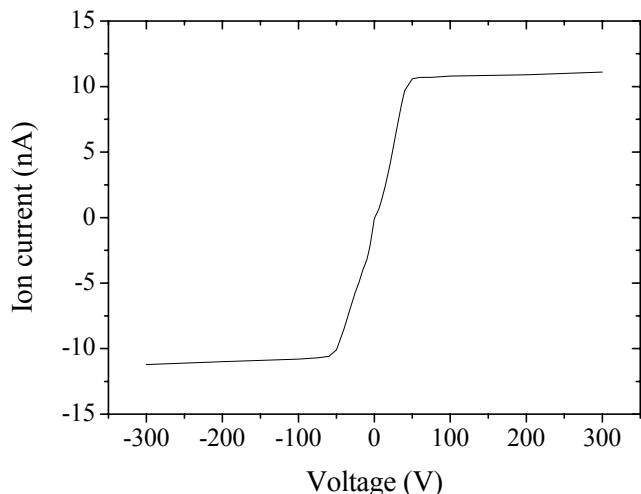


Fig. 7. Dependence of the ion current on the applied voltage @ 7ml/min sample gas flow

Fig. 8 shows the sample gas flow versus ion current. Only within the range from 3ml/min sample gas flow up to 4.5ml/min the characteristic possesses the linearity, which can be expected from the carbon atom concentration. Below 3.5ml/min sample gas flow, incomplete mixture is presumed to lower sensitivity [1]. Above 4.5ml/min, the decreasing flame temperature, due to cooling by the sample gas, causes decreased sensitivity until at 13ml/min sample gas flow the flame is even extinguished.

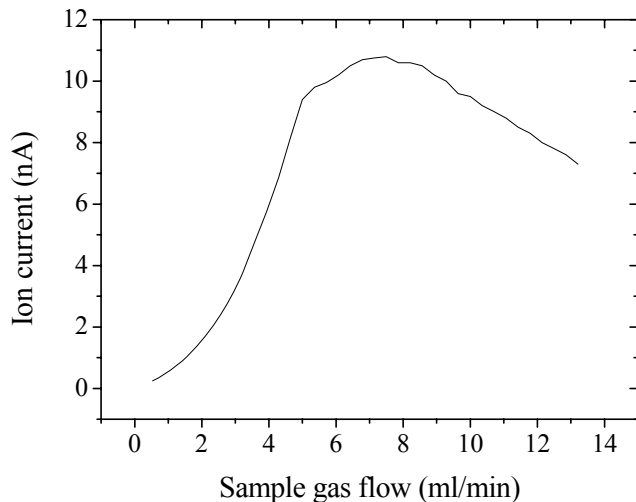


Fig. 8. Dependence of the ion current on the sample gas flow @ 100V

## VI. CONCLUSIONS

In this paper a planar  $\mu$ FID with integrated guard electrode has been proposed. However, measurements with the proposed system have not been performed yet. Instead, preliminary measurements were performed with a planar  $\mu$ FID without integrated guard, of which the measurement electrodes were mechanically separated to exclude any leak currents. The preliminary results show expected FID behavior with ion current saturation at 50V only. Therefore, ion current saturation can be expected below 10V for the planar  $\mu$ FID with integrated guard electrode, which is about a factor 10 smaller than it is for conventional FIDs.

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