

Design and Fabrication of a Micro-size Thermionic Ionization/Flame Ionization Detector for Gas Phase Chemical Analytes

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Abstract—A simple, MEMS base micro-chemical detector utilizing the principles of gas ionization, has been designed and fabricated. The device contains a polysilicon micro air-bridge heater structure with integrated polysilicon electrodes. The design of the devices allows it not only functions via thermionic emission, but also via chemi-ionization if a proper Pt catalyst is applied and it is operated in an environment containing hydrogen.

When properly biased the device has been shown to heat to high temperatures where thermionic emission can begin to occur. Hydrocarbon chemicals in the gas phase have shown to ionize, via thermionic ionization and have been collected, producing a measurable current signal.

Index Terms—Chemical detection, gas chromatography, ionization, MEMS, micro-heater, sensor.

I. INTRODUCTION

The need for portable chemical detection has grown more important in our world today. A device that is sensitive to multiple chemical analytes is important when analyzing unknown substances and would be useful in national security, detective forensics or the food and health industry. MEMS based technology has made such sensor feasible to fabricate.

The design, fabrication, and testing of a micro-sized gas phase chemical detection sensor that can operate either via thermionic emission or flame ionization has been designed and fabricated. The thermionic ionization detector (TID) or flame ionization detector (FID) could be used in portable chemical detection systems, involving gas chromatography. A micro-size sensor of this sort requires less power while possibly providing nearly the same sensitivity of chemical detection as compared to its conventional, macro-sized counterparts. Also, the development of such a device, using silicon-based

micromachining techniques, shows the feasibility of a mass production of the sensor.

The two modes of the sensor are similar in operation. The TID operates under the principles that when a filament is heated to high enough temperatures, thermionic emission of electrons will occur. When in the presences of a gas analyte the properties of the emission will change, causing ionization, creating a detectable signal. Coatings or catalyst can be used to change the sensitivity of the device. Typical the TID is most sensitive to nitrogen or phosphorus containing compounds. The FID works in the presence of air and hydrogen. When the heater filament is coated with a catalyst, an oxy-hydrogen flame is produced. When gaseous analytes pass through this flame, they are ionized. The ions are then collected by the electrodes producing a measurable signal. Because of the oxy-hydrogen flam FID is extremely sensitive to hydrocarbons.

II. GAS CHROMATOGRAPHY

Gas chromatography (GC) is the method use to separate gaseous mixtures. A GC process of separations is typical some sort of column, often a glass capillary, which a gaseous mixture flows through. Three main factors determine the separation of a mixture: column length, time, and a molecules affinity to the column material (the stationary phase). The molecules affinity will actually cause the separation. Its affinity is how well the molecule adsorbs and desorbs for the column walls. The column length and time which the molecule passes trough the column will help to separate the distance between the species and the leave the column, allowing for more discrete detection. Often times these column walls are coated with a film or pack with beads to help to change the affinity properties.

By speeding up the separation process the peaks of the GC output will not be as defined. The spread of the peak will be larger and over lap with other molecules in the mixture. Thus, a fast response detector is required; if the high speed chromatography is to be done.

III. THEORY

A. Thermionic Ionization Detector (TID)

When a material is heated to very high temperatures, enough energy can be imparted to cause emission of electron. Because of the large amount of thermal energy, surface molecules, on

Manuscript received May 14, 2004. This work was supported in part by the Rochester Institute of Technology, Department of Microelectronics Engineering.

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the heated substance, may absorb that energy and use it to emit an outer shell electron. Thermionic emission current is governed by several parameters, including temperature, T , work function or ionization potential of the material, and an emission constant, A (Richardson's constant).

$$J = AT^2 e^{\frac{-\phi/k}{T}} \quad (1)$$

If a gaseous analyte is in the presence of a hot surface that is emitting electrons via Thermionic emission, it can be ionized. The emitted electrons can collide with the analyte, removing an electron. In order to do this, the electron emitted must have a higher energy than the binding energy that is holding the electron on the analyte molecule.

Thermionic ionization may also occur of a gaseous analyte via other mechanisms. If the temperature is high enough, a molecule brought into the presence of the high temperature may self ionize. Essentially, the larger amount of thermal energy will be adsorbed by the molecule, causing it to emit an electron.

Once an analyte is ionized, it has net charge associated with it, making it susceptible to an electric field. Thus, if the ionized molecule is in-between electrodes, one with a bias, a force can be imparted on it. One of the plates can be left floating and used for collection. Depending on the bias on the other electrode, electrons or ions can be forced to the collection electrode. This creates an ionic current which can be measured. As GC eluents become present to the detector, they become ionized and the biased electrode forces the ionized gas to a collector creating ionic current. This current can be measured, denoting a signal of a chemical species being present. Figure 1 shows the general schematic of the TID.

The longer the ions take to reach collector electrode, the more recombination takes place. Thus, the greater the distance the electrodes are from one another, the lower the voltage produced for signal (Ref. [1]). The applied voltage needs to be adjusted depending on electrode spacing. Performance is not necessarily improved or comprised because electrode spacing as long as the voltage is adjusted.

Though theoretically the TID can detect any gaseous chemical substance if enough energy is present, it is typically most sensitive for hydrocarbons, nitrogen, and phosphorus containing compounds.

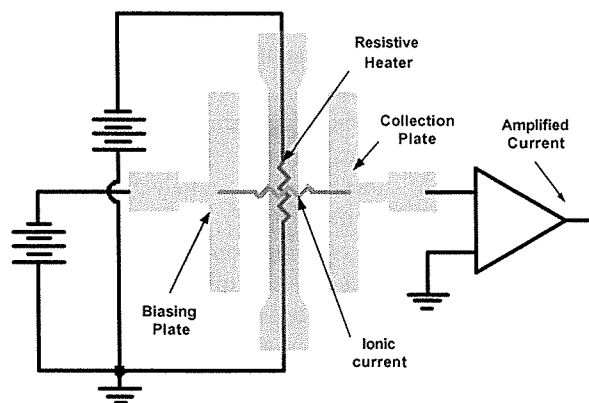


Figure 1: Schematic of the TID operation

B. Flame Ionization Detector (FID)

An alternate mode of the TID is the flame ionization detector. It works on the same principles as the TID, but the method of ionization differs. If the heat source of the TID is coated with platinum or a platinum base coating and put in the presence of a hydrogen ambient, catalytic combustion will occur. If a GC eluent is passed through the combustion zone, ionization of that species will occur. This mechanism is known as chemi-ionization. This form of ionization is very sensitive to hydrocarbons. This is the result of the reaction of CH with O as shown below:



The FID is characterized as having very high sensitivity of these types of molecules and a working range of many orders of magnitude.

IV. DETECTOR DESIGN AND FABRICATION

For the detector design, MEMS surface micromachining techniques were incorporated to fabricate a simple micro polysilicon air-bridge heater filament with integrated polysilicon electrodes. The heater was designed to operate at relatively low voltages, around 15 to 20V and produce temperatures upwards of 900°C. Electrode spacing from the heater varied from 50 to 500µm. Spacing was arbitrarily chosen because biasing would determine collection of the ions. Aluminum was used for contact to the polysilicon.

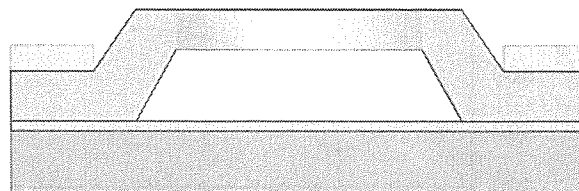


Figure 2: Cross section of TID micro-structure

Fabrication of the device consisted of three mask levels. First a LPCVD Si_3N_4 film was deposited to create an insulating barrier from the silicon substrate. Then 3µm of PECVD oxide was deposited and patterned. This layer is used as the sacrificial layer. Two microns of LPCVD polysilicon was then deposited

and doped using N-type spin-on-glass. Aluminum was deposited on top of the polysilicon and patterned with the heater and electrode structures. The aluminum was used as a hard etch mask to etch the polysilicon in RIE plasma system. The remaining aluminum was then pattern and etch to form contacts on the polysilicon heaters and electrodes. Finally the structures were released in a 49% HF etch.

Because the heaters were 3mm long, they often stuck to the surface after release. This was due to capillary forces from the rinse after the release. To alleviate this problem, a DI water / IPA / DI wafer / IPA rinse was incorporated followed by a 200°C bake on a hot plate to suspend the structures.

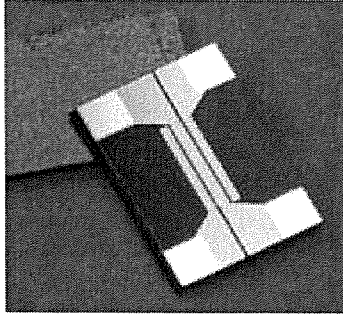


Figure 3: Fabricated straight filament micro-heater with integrated electrodes. The filament is 3000 μ m by 300 μ m. The electrodes are 100 μ m from the heater. The dimensions of the die are 4.5mm by 6.5mm

V. TEST SETUP

A. Thermal Characterization

Once suspended structures were fabricated, thermal characterization was performed. This was done by measuring the change of resistance of the heater structures on with temperatures. Resistance was measured at various temperatures ranging from 20 to 325°C

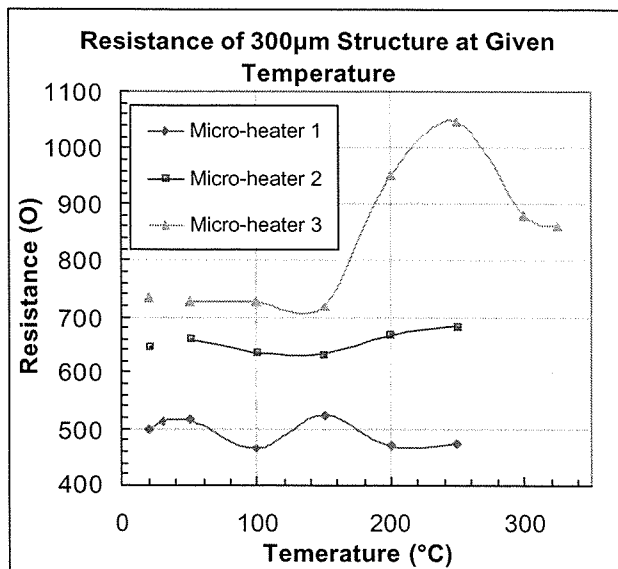


Figure 4: Change in resistance versus temperature. Fluctuation in the resistance is due to both increased number of intrinsic carriers and thermal expansion of the polysilicon.

Normally resistance is expected to increase with temperature. However, both increasing number of intrinsic carriers in the polysilicon and thermal expansion seem to cause a “tug-of-war” effect with the structure resistance. This causes the resistance to go up and down with temperature.

From the resistance data, the temperature coefficient of resistance (TRC) was determined. The average TCR was found to be 0.000209/°C for the 3000 by 300 μ m structures. Using this value and applying a 46V bias across the heater, an estimated temperature of about 878°C was determined. The bias used was larger the original designed because the resistivity of the polysilicon came out higher during fabrication than originally assumed.

B. Pneumatic setup

The Pneumatic setup for introducing chemicals to the micro TID is shown below.

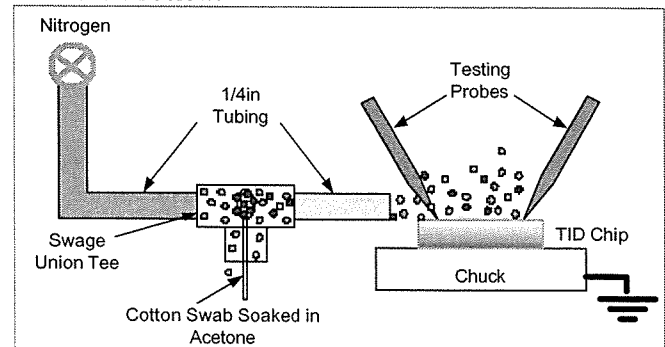


Figure 5: Setup for introduce a chemical analyte to the device under test

Nitrogen was used a carrier gas to introduce chemicals to the detector. A stream of approximately 100mL/min was used. Acetone was the analyte chosen for the chemical detection test. A swab, soaked in acetone, was inserted into the nitrogen stream and the vapors were carried to the device. The device was heat up to above 800°C and a 100V bias was applied to one of the electrodes. A HP4145 parameter analyzer was used to both apply the electrode biasing and to measure the ionic current produced.

VI. RESULTS

Using the above test setups, acetone analyte peaks were measured, which simulated the output of a gas chromatograph column. Results of the first run can be seen in the figure 6 below:

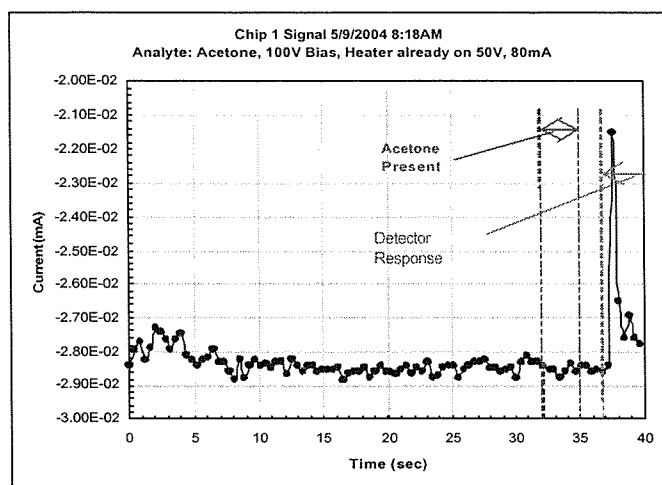


Figure 6: Detection of an Acetone peak

Detection of an acetone peak, in figure 6, shows that a micro-sized TID can be used for analyte detection. The shape of the peak is similar to that of what is typically found in conventional GC setups. The time the analyte was present for detection is indicated on the plot. The time difference of when the analyte was present and the time for signal has not to do with the speed of the detector's response but rather the time it took for the chemical to reach the detector.

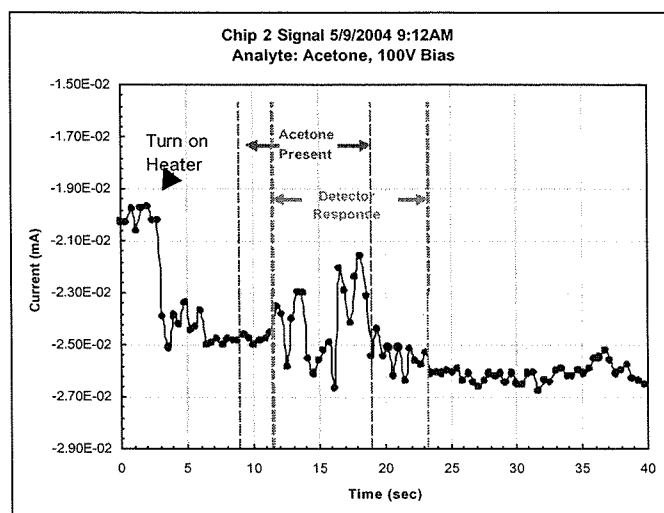


Figure 7: Acetone signal with initial peak measure during heater activation

In figure 7, it is seen that a signal for acetone was repeated. However, what is interesting to note is that there is an initial signal in the beginning of the plot. This initial peak occurred when the micro-heater was activated by turning on the power supply. Surface contamination on the heater filament it self ionized, and was collected by the electrodes creates an initial peak. However, after a few moments of warm up it is observed that the signal did settle down. After the acetone signal, it is further observed that the background noise becomes less. This may be link to the further removal of the initial surface contamination. It may be necessary for a few moments of temperature stabilization by the device. This could be done by

just cycle heat the filament momentarily then the heating to the desired operation temperature.

VII. CONCLUSION

Successful fabrication, using MEMS micromachining techniques, of a micro thermionic ionization detector utilizing a polysilicon, air-bridge heater with intergraded polysilicon electrodes was accomplished. The device was shown to reach temperatures above 800°C when biased properly. Using a nitrogen carrier gas, detection of a significant acetone signal was demonstrated. The many signals attained had very similar characteristics to those attain from a conventional gas chromatography detector having a sharp rise and slightly slower fall off.

Further work will include demonstration of detection of multiple peaks when the detector is utilized with a gas chromatograph and to determine the lower detectable limit of the TID.

ACKNOWLEDGMENT

The author would like to thank Dr. Lynn Fuller, of the Rochester Institute of Technology for his advising of the progress of the TID project. He would also like to thank Dr. Ronald Manginell of Sandia National Laboratories for his guidance and suggestions for the project.

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