CONDUCTIVITY PULSE TIME-OF-FLIGHT FLOW SENSOR FOR SUB-MICROLITER/MINUTE FLOW RATES

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ABSTRACT

A microfluidic flow sensor capable of measuring liquid flow rates ranging from 10-2000 nL/min was fabricated in a glass chip with integrated metal electrodes. Flow rate is determined by measuring the flight time of an ion pulse introduced by electrolysis at a pair of electrodes inside the channel. The resulting conductivity increase is detected downstream by another electrode pair. Flight times are advection dominated due to rapid mass transfer of ions from the electrode surface to the bulk flow. Potential applications include microfluidic pump control for high-pressure liquid chromatography and other micro total analysis systems.

KEYWORDS: flow sensor, microfluidics, time-of-flight, electrodes

INTRODUCTION

Several types of flow sensors have been developed to provide feedback in microfluidic systems, including sensors which measure the pressure drop over a restriction and those based on the dispersion of a thermal pulse. We have developed a sensor based on the time of flight of an ion pulse generated by electrolysis at an electrode pair (see schematic in Figure 1). The advantage of the conductivity pulse time-of-flight (CP-TOF) sensor over microfabricated thermal anemometers is that unlike a thermal pulse, an ion pulse cannot diffuse into the system walls. Therefore, thermal isolation strategies such as thin walls with air gaps [1] are not necessary, enabling the sensor to be readily integrated into thick-walled high-pressure systems. The CP-TOF sensor is also relatively insensitive to viscosity variations, either from composition or temperature fluctuations. In contrast, flow sensors based on viscous drag, such as those that detect a pressure drop over a restriction [2], require fluid-dependent calibrations. However, the CP-TOF sensor requires fluids that support rapid electrolysis in response to a short, high-voltage electrical pulse. In addition, the ion pulse must persist long enough to reach the detector even at the slowest flow rates, which is not the case in strongly-buffered solutions. Flow rates above 1000 nL/min have previously been measured in strongly-buffered solutions using electrodes to detect the flight time of an injected oxygen pulse rather than an ion pulse [3].

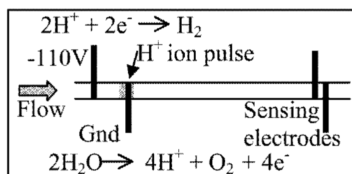

Figure 1: Ion pulse generation

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Fluids of interest for chromatography that were used in the CP-TOF sensor include 5 mM aqueous tris(hydroxymethyl)aminomethane (TRIS) buffer, pH 8, and aqueous/organic mixtures of water/acetonitrile containing 0.1% trifluoroacetic acid.

FABRICATION

Devices were fabricated by wet-etching glass wafers, depositing metal electrodes, and thermally bonding glass cover plates containing drilled vias. The process flow is shown in Figure 2.

Deep channels were first created by a 50 micron etch in concentrated hydrofluoric acid (HF) through a lithographically patterned silicon hardmask (Figure 2a). Then, new areas were opened in the hardmask to define shallow channels for the pulse flight tube. These areas, and the previously etched channels, were etched 5 microns in the HF solution (Figure 2b). Next, thick photoresist (15 microns) was used to define the electrode pattern on top of the silicon. The silicon in the electrode areas was removed by plasma etching, then a 200 nm countersink was created for the electrodes by etching the glass in dilute HF (Figure 2c). Then, a 20 nm titanium adhesion layer and a 180 nm thick platinum film were deposited by sputter coating (Figure 2d). Excess metal was removed by lifting off the photoresist in an ultrasonically agitated acetone bath (Figure 2e). Etched wafers and drilled cover plates were briefly dipped in dilute HF to relieve stress caused by machining, then cleaned by immersion in Piranha solution (4:1 H_2SO_4:H_2O_2) at 100 C. Wafers were further cleaned by immersion in concentrated sodium hydroxide, which also removed the silicon hardmask, then rinsed with deionized water and dried in a spin-rinse dryer. Cleaned wafers were thermally bonded in a furnace at 610 C for 5 hours (Figure 2f), then diced into chips containing two sensors. Fluid connectors were bonded over via holes with epoxy, and devices were attached to chip carriers for electrical connections. Figure 3 is a photo of a finished device.

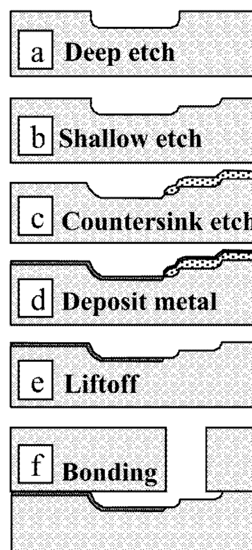

Figure 2: Process flow

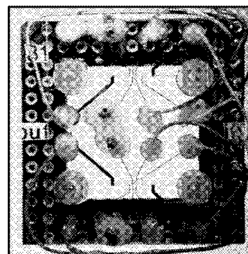

Figure 3: Top view of double flow sensor device. (3.3 x 3.3 cm)

FLOW SENSOR OPERATION

During operation with aqueous acidic or neutral fluids, the high voltage electrode is pulsed at -110V for 1 ms. The adjacent downstream electrode is grounded. Ions generated by water oxidation at the ground electrode move downstream with the flow and

are sensed as a conductivity increase at another pair of electrodes near the channel exit. Later, there is a conductivity decrease due to ion depletion at the –110 V electrode. Because of dispersion, the depletion peak amplitude is at most only 1/3 that of the ion peak. Conductivity is measured by using a lock-in amplifier circuit to monitor the amplitude of the current as a 30 kHz, 1 V peak-to-peak voltage signal is applied between the sensing electrodes. To eliminate DC electronic drift, the signal is passed through a differentiating filter. The TOF is defined as the time between the start of the high voltage pulse and the conductivity maximum.

By using different pairs of pulse electrodes for slow, medium, and fast flow rates, the flow rate can be measured over three orders of magnitude, with TOF measurements ranging from 20 ms to 200 ms. Representative conductivity traces for 5 mM TRIS buffer are shown in Figures 4a (slow range), 4b (medium range) and 4c (fast range).

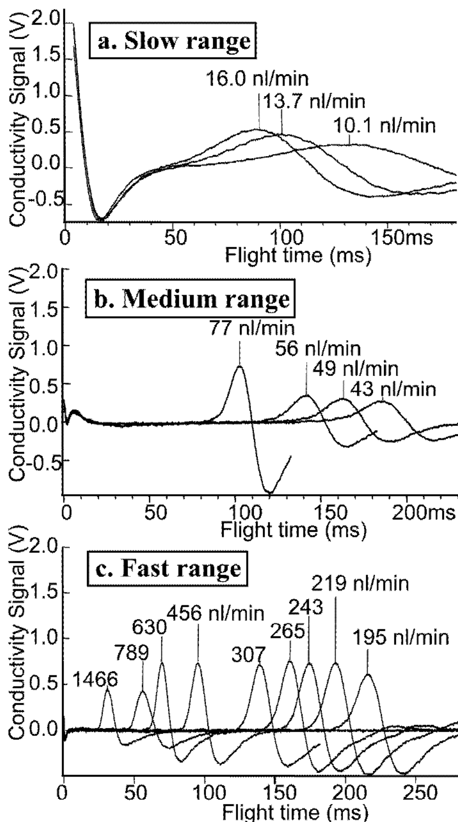

Figure 4: Conductivity traces for slow (a), medium (b), and fast (c) settings

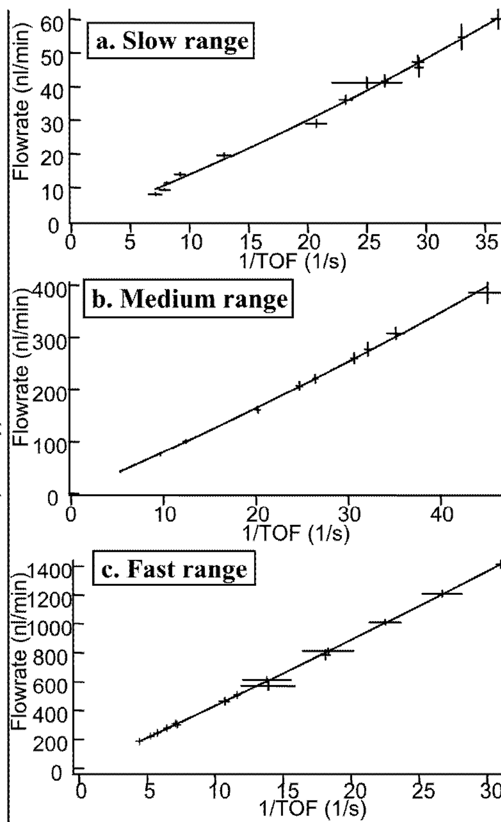

Figure 5: Flowrate vs. 1/TOF for slow (a), medium (b), and fast (c) settings

Calibration was performed by timing the outflow of liquid from the chip into a glass capillary of known volume. For flow rates between 10 nl/min and 600 nl/min, a Milligat pump (Global FIA) was used to deliver fluid to the sensor, and for 400 nl/min to 2000 nl/min, a syringe pump was used. The nominal flow rate of the pumps was within 10% of the capillary flow rate measurement. Calibration curves for the three ranges in 5 mM TRIS buffer are shown in Figures 5a (slow range), 5b (medium range) and 5c (fast range), with flow rate and flow rate error bars given by the capillary measurement method, and TOF error given by the standard deviation of 100-1000 flight time measurements. For TRIS buffer, the CP-TOF flow rate measurement error is typically 1% of the flow rate. At the lowest flow rate of 10 nL/min, the error is ~5% of the measured flow rate. Electrolysis from the brief voltage pulse does not produce visible or electrically detectable bubbles, nor bulk solution pH changes.

CONCLUSIONS

The CP-TOF sensor works best in aqueous solutions with low buffer concentrations (<10 mM). It is easily integrated into the microfluidic fabrication process, and has been operated at a maximum pressure of 1200 psi in glass chips. Because the conductivity sensor detects the presence of bubbles and particles as well as the ion pulse, solutions should be filtered and degassed. With the three-range system, flow rate measurements from 10 to 2000 nl/min can be acquired at a minimum rate of 5 Hz. For these reasons, the CP-TOF sensor is suited to providing flow rate feedback in microscale systems where high-purity reagents are dispensed at high pressures.

ACKNOWLEDGMENTS

We wish to acknowledge financial support from the Waters Corporation and discussions with Keith Fadgen at Waters, advice on integrating the flow sensor with pumping systems from Ken Patel, the microfluidic packaging contributions of Ron Renzi and Judy Rognlien, and the microfabrication expertise of Bill Kleist, Sue Jamison, and George Sartor.

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