

MONOLITHIC MEMS VACUUM VALVES FOR MINIATURE CHEMICAL PRE-CONCENTRATORS

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ABSTRACT

A monolithic pneumatic valve is reported for use in a miniature chemical pre-concentrator. The valve comprises a perforated diaphragm above a substrate with offset perforations. The diaphragm is closed electrostatically, can be coated with adsorbent material for collecting the analyte of interest, and heated ohmically to desorb the analyte into the analytical system. The valve supports a high flow rate when open, along with the ability to maintain closure against over one bar of pressure, allowing its use with vacuum based instruments such as mass spectrometers. The fabrication process is described, and pneumatic and thermal performance are reported.

KEYWORDS

Mass spectrometer, pneumatic valve, bonded silicon

INTRODUCTION

Preconcentrators are well established devices for enhancing the sensitivity of detection instruments. A typical preconcentrator comprises a porous or perforated structure which inherently, or by the addition of a suitable coating material, absorbs the substance of interest from a sampled gas flow. The material is then desorbed, usually by heating, into a much smaller gas volume than that sampled, and the resulting concentrated sample is injected into an analysis instrument.

MEMS provides a suitable method for producing miniaturized pre-concentrator structures, and a number have been reported. Sandia National Laboratories have developed coated diaphragm pre-concentrators with integrated heating elements, which allow very rapid desorption, and more recently have also reported flow-through devices which increase the adsorption surface area [1]. These devices were designed for use with micro-fabricated gas chromatography columns, as were the devices of Zellers et al. [2]. Martin et al. developed a preconcentrator based on a perforated Si diaphragm, and demonstrated its operation as an input to an ion mobility spectrometer [3]. The flow of the sampled and injected gases must be controlled and timed, typically using valves. If these are also micro-engineered, a very small dead volume can be achieved, maximizing the concentration ratio of the device [4].

By integrating the valve and pre-concentrator into a single structure, the ultimate miniaturization can be reached. Fig. 1 illustrates our device concept: a perforated

silicon diaphragm floats above a substrate with offset perforations, such that pulling the diaphragm down electrostatically closes the valve. The diaphragm can be coated with a patterned adsorbent material, and heated for desorption by passing a current laterally across it.

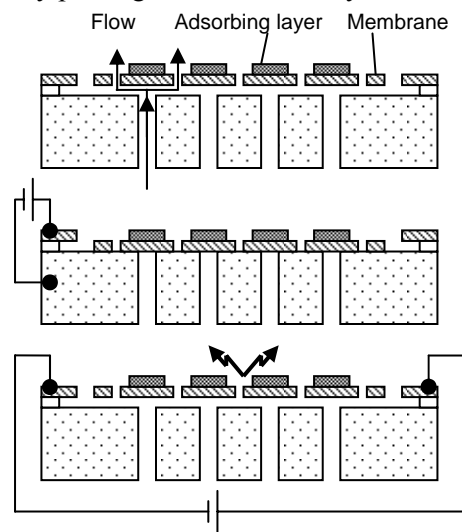


Figure 1: Integrated pre-concentrator valve in (top to bottom) sampling, closed and desorption states.

By assembling four of these devices in the configuration shown in Fig. 2, with one valve pair controlling the sampled inlet and exhaust, and the other the flush gas (if required) and injection, a complete pre-concentrator is achieved.

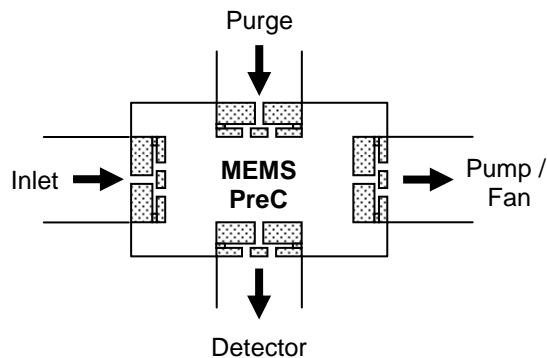


Figure 2: Four-valve pre-concentrator assembly.

In the sampling mode, inlet and pump valves are open, the other valves are closed, and air is drawn through the device at high rate. During this sampling phase it may be necessary to heat the overall device to a modest level to reduce adsorption on surfaces other than the inlet valve coating. During the analysis phase, inlet and fan valves are

closed and the detector valve is open, the inlet valve diaphragm is heated to release the analyte, which is then drawn into the detector either by diffusion or by provision of a carrier gas through the purge inlet.

The requirements for the valves depend strongly on the analysis instrument. For ion mobility spectroscopy (IMS) or gas chromatography-mass spectrometry (GC-MS), as used with previously reported MEMS pre-concentrators, the instrument inlet is at atmospheric pressure, so that the valves will not usually need to withstand a large differential pressure. Recently, quadrupole mass spectrometers (QMS) have been miniaturized using MEMS approaches [5], and interfacing pre-concentrators directly to these is highly attractive. Since QMS operates at vacuum, this requires that the valves in the system of Fig. 2 can be held closed against one bar of differential pressure with low leakage. Also, to allow a large air volume to be sampled, the same valves must allow a high flow rate at an acceptable driving pressure.

FABRICATION PROCESS

The MEMS valves are generated with a two-mask process at wafer scale. The process is summarized in Figure 3a to 3f. The starting point is a double side polished bonded silicon-on-insulator (BSOI) wafer with a device layer of thickness 30 μm and with low resistivity. An oxide thickness of 4 μm separates the device layer and substrate handle layer. Substrates of thickness 500 μm and again of low resistivity were used. The BSOI wafer is initially thermally oxidized to grow about 1 μm SiO_2 on the device and handle layers (Fig. 3a). Photoresist is then spin coated and patterned consecutively on the two sides (Fig. 3b), and the resist is used to pattern the oxide layer by dry etching. These patterns are transferred into the corresponding silicon layers using a Surface Technology Systems Single Chamber Multiplex inductively coupled plasma (ICP) etcher, operating a variant of the cyclic etch-passivate process based on SF_6 and C_4F_8 developed by Robert Bosch GmbH [6] (Fig. 3c). The resist mask is then removed using a commercial wet resist stripper followed by oxygen plasma. Front to back alignment is carried out using a Quintel IR-4000 mask aligner with through-wafer infrared illumination.

Once the valves have been patterned on both sides, the die are singulated. The buried oxide is then removed by HF vapor etching using a commercially available system [7]. Once complete, the device handle layers are physically released from each other to form the basic structure of the gas valve (Fig. 3d). Electrical isolation between the device and handle layers is achieved by re-oxidizing the device at 1100°C for 48 hours (Fig. 3e). Finally, contact areas to both layers are patterned into the oxide, and electrical contacts are attached (Fig. 3f).

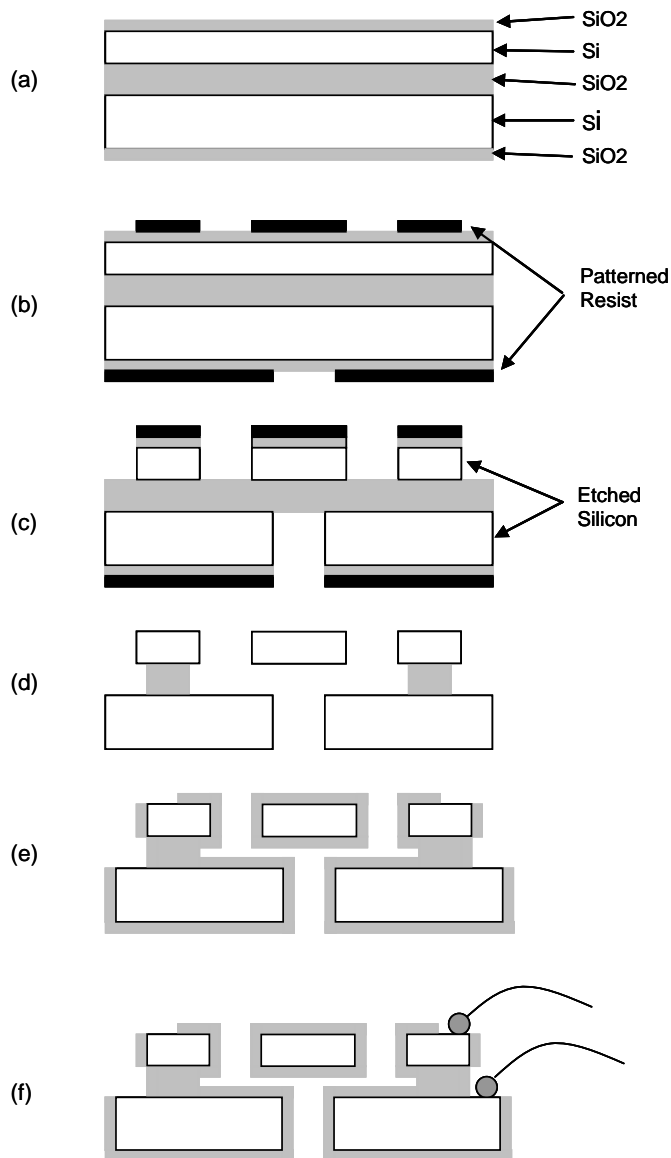


Figure 3: Fabrication process steps as described in the text.

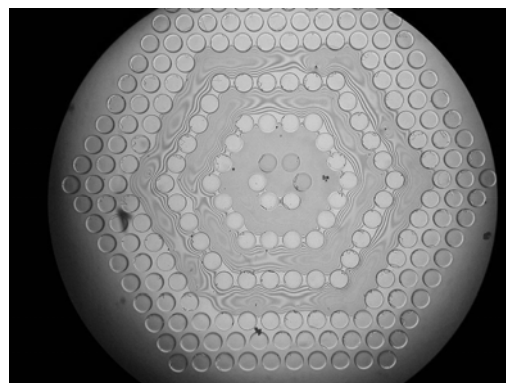


Figure 4: Diaphragm surface with adsorbent polymer coating.

Fig. 4 shows a completed valve from the diaphragm side. A polymer adsorbent layer has been patterned in the central region between the perforations by inkjet deposition. Fig. 5 shows a mounted device on a printed circuit board.

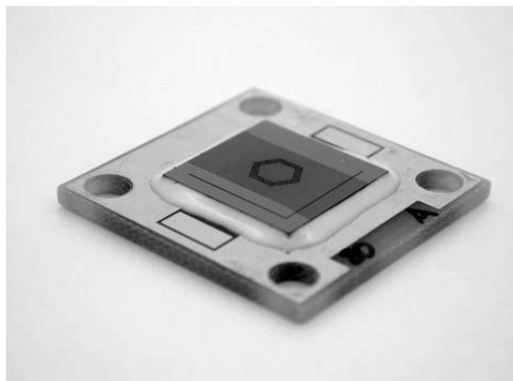


Figure 5: Valve mounted on printed circuit board.

EXPERIMENTAL RESULTS

Figure 6 shows the high pneumatic performance achieved. Devices were mounted in a pneumatic test rig with flow and pressure measurement, and the flow rates measured as a function of differential pressure for open and closed states. In the closed state, the valve leakage is below the limit of measurement of 0.01 sccm, for differential pressures up to 1.1 bar. In the open state, flows up to 10 l/min are obtained for 500 mbar forward pressure, yielding an open to closed flow ratio of at least 10^6 . This can be compared to a flow of 0.3 l/min at 500 mbar in [4]. About 100 mbar forward pressure is required in the open state to achieve substantial flow. In both open and closed states the valves are oriented so that the differential pressure tends to open them.

In a simple approximation, the maximum concentration factor achievable in a pre-concentrator is given by the total sampled volume divided by the “dead volume” of the device. In practice this is limited principally by two considerations: firstly, the collection efficiency for the analyte of interest will be below 100%, and secondly, the volume or surface area of sorbent material will place an absolute (saturation) limit on the amount of analyte that can be collected, so consequently the concentration factor cannot be increased limitlessly simply by extending the sampling time. For a device integrating four valves of the type presented here, with sub-mm inter-valve spacings, an enclosed volume of about 0.1 cc should be achievable, which then sets the minimum dead volume. For one minute of sampling at 10 l/min, this suggests a maximum volume ratio as high as 10^5 , which could in principle provide a concentration factor above 10^4 if saturation is not reached.

Insensitivity to dust contamination has also been demonstrated. To characterize the trapping of dust particles by the device, a controlled flow of air from an office environment was presented to a particle size analysis instrument, with and without the valve in the flow. As can be seen in Figure 7(a), a significant fraction of particles above 1 μm are trapped in the device. The pneumatic performance of otherwise equivalent devices was then

measured for nominally clean valves (indicated as CR), and valves having passed 3 and 30 liters “dirty” air. As can be seen in Figure 7(b), no change in open flow rate, or closed leakage, was detected, despite the presence of trapped dust particles.

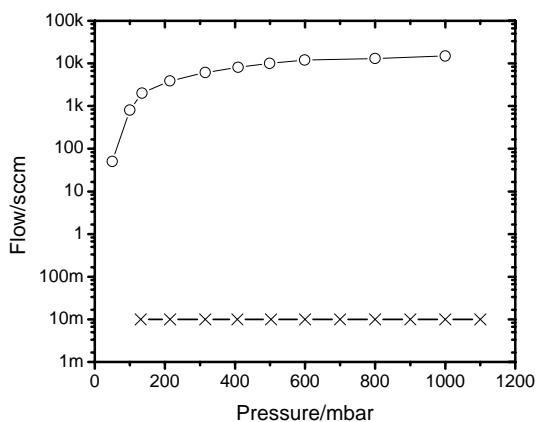
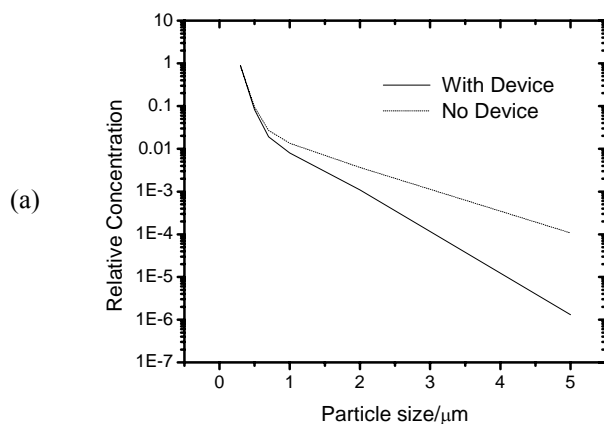
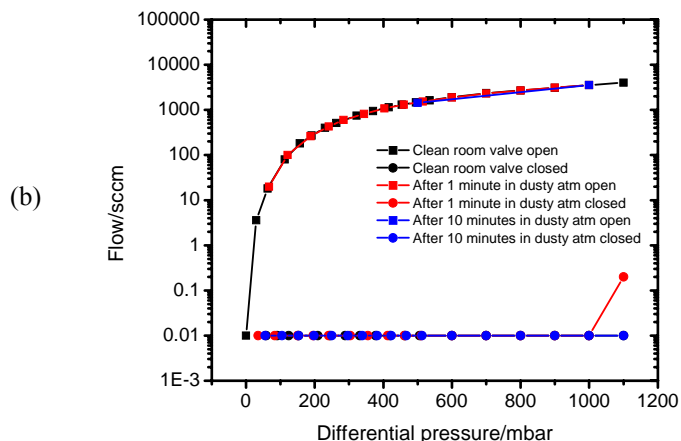


Figure 6: Pneumatic performance of valve in open (o) and closed (x) states.



(a)



(b)

Figure 7: (a) Dust particle size distribution for air before and after passing through valve; (b) flow vs. pressure for valves before and after passing dusty air as indicated.

Thermal performance was also evaluated. Figure 8 shows a thermal camera image of the diaphragm with the

heating current supplied. Reasonable temperature uniformity is achieved, and the target desorption temperature of 170°C could be reached across most of the surface. Uniformity is acceptable across most of the surface, although lower temperatures are seen at the edges in particular. Altering the geometry offers the possibility of improving the temperature uniformity by altering both the electrical current flow and the heat flow across the diaphragm.

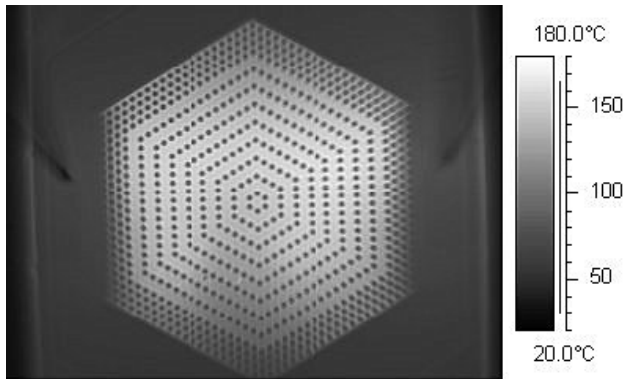


Figure 8: Thermal image of valve with heating current applied.

The thermal response time was also measured, as shown in Figure 9. Initially a high fixed heating current is applied; the current is then stepped down in increments at 5 second intervals. In this case the target temperature of 180°C is reached in about 5 s, and the difference between the spatial maximum and average temperatures for the diaphragm is about 10°C. Closed-loop control of heating should allow both more rapid stabilization, and reduction of the overshoot amplitudes.

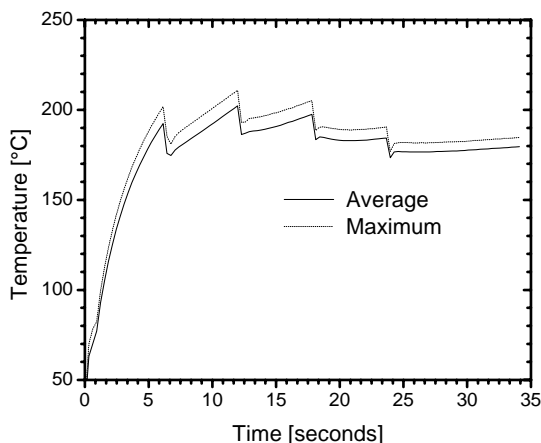


Figure 9: Thermal response of heated valve.

CONCLUSIONS

In summary, monolithic pneumatic MEMS valves have been demonstrated, with integrated surface sorbent coating and surface heating capability. Compatibility with vacuum interfaces is shown by the low leakage under a forward

bias above one bar, and a high flow rate when open, for forward pressures above 100 mbar, is achieved. Ohmic heating provides diaphragm temperatures up to $\approx 180^\circ\text{C}$ within several seconds, with acceptable spatial uniformity.

Further work is focused on demonstrating full preconcentrator functionality for various analytes and analytical instrument types.

ACKNOWLEDGMENTS

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