Silicon based quadrupole mass spectrometry using microelectromechanical systems

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The conventional quadrupole mass spectrometer (QMS) arrangement uses circular metallic rods as the mass filter excited electrically at voltages up to 1 kV depending upon the application. If the size and voltages can be reduced then the range of applications for QMS instruments would increase. The application of microelectromechanical systems (MEMS) technology allows the fabrication of submillimeter versions of such structures. In this article the development of a miniature QMS is reported in which the conventional rod arrangement has been replaced with a microengineered version. The structure is made in silicon with metallized specially drawn glass fibers of length 20–30 mm and diameter 0.5 mm to act as the quadrupole rods. This is about one order of magnitude smaller than most conventional QMS filters, with the potential for further reduction in size. The MEMS mass filter was mounted onto a commercial ion source, which was in turn attached to a vacuum flange and supplied by an electronic drive circuit at 6 MHz. Mass spectra in the range 0–50 amu for a range of operating conditions have been obtained indicating a linear mass scale and a best resolution at 10% peak height of around 30. The use of pole bias applied to the rods is shown to be beneficial. Reliable QMS operation was obtained up to a pressure of 10^{-2} mbar. [DOI: 10.1116/1.1359172]

I. INTRODUCTION

In recent years there has been an increasing drive towards miniaturization in mass spectrometry. Miniature versions of time of flight, Wien filter, magnetic sector, quadrupole ion trap, and ion cyclotron resonance mass analyzers have been made.[1,2] One of the major forces behind these developments is the space program where small size and low weight are primary considerations. Microelectromechanical systems (MEMS) made using integrated circuit fabrication techniques offer the possibility of order of magnitude decreases in spectrometer size and are thus attracting considerable interest.

Quadrupole mass spectrometers (QMS) have found a wide range of applications in the medical field, chemical process industries, and more recently in process monitoring in semiconductor fabrication plants where ultraclean processes for ultralarge scale integration are a priority. QMS based on cylindrical rods for the mass filter are now highly developed and successful.[3] In recent years economic methods of precision mass analyzer assembly have been devised, however, the mass filters are still relatively large and require large drive voltages at radio frequencies (rf).[4] If the size and weight of such instruments can be reduced further by MEMS fabrication then a number of advantages follow.

- (i) The cost of manufacture falls since in principle a batch of several mass analyzers can be made simultaneously on a single silicon wafer. Potentially the MEMS QMS can become a ''throw away'' instrument.
- (ii) The small size means that the ion mean free path length can be reduced which allows operation at higher pressures.
- (iii) The small size/higher pressure combination avoids the use of an expensive and bulky vacuum pumping system.
- (iv) Low power battery operation is possible since the electrode voltages can be reduced. The possibility emerges of a fully integrated MEMS QMS driven by associated on chip electronics.

Such advantages mean that the range of applications should increase. In this article we give a description of the fabrication, operation, and performance of a silicon based quadrupole mass spectrometer with the mass filter made using MEMS technology.

II. FABRICATION

A. Mass filter design

An ideal quadrupole mass filter consists of four parallel electrodes with hyperbolic sections. These carry potentials $\pm\phi_0/2$ and establish a two-dimensional potential variation in the $x-y$ plane of the form

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$$\phi(x,y)=\phi_0(x^2-y^2)/2r_0^2, \tag{1}$$

where r_0 is the radius of the circle touching the equipotentials $\phi=\pm\phi_0/2$. The equation of motion for ions moving in the x direction is $md^2x/dt^2=-e\partial\phi/\partial x=-e\phi_0 x/r_0^2$, where e and m are the charge and mass of the ion, respectively. When the time variation of the potential supplied to the rods is $\phi_0(t)=U-V\cos(\omega t)$ where $\omega=2\pi f$ and U and V are constant potentials, this reduces to

$$d^2x/dt^2+(e/mr_0^2)[U-V\cos(\omega t)]x=0. \tag{2}$$

However, because of the difficulty of machining electrodes with a hyperbolic cross section, cylindrical rods are normally used. Experiments have shown that the best approximation to the field of Eq. (1) is obtained when the electrode radius r_e is chosen so that $r_e=1.148r_0$. Numerical solutions of the Laplace equation have confirmed this result, but show that a grounded shroud around the electrodes alters the optimum radius.[5] Before developing a microengineered equivalent of a conventional quadrupole, size scaling was considered as follows. The number of cycles of the rf field experienced by an ion traveling through the mass filter is[6]

$$n\approx fL/v=fL\sqrt{(m/2eV_z)}, \tag{3}$$

where L is the length of the lens and V_z is the axial ion energy, measured in electron volts. It has been shown experimentally for conventional QMS with circular electrodes that the mass resolution at 10% peak height depends on n according to

$$m/\Delta m\approx n^2/20\approx f^2L^2m/40\ \ \mathrm{eV}_z. \tag{4}$$

So that the uncertainty in mass is

$$\Delta m\approx 40\ \ \mathrm{eV}_z/f^2L^2\approx 3.854\times10^9 V_z/f^2L^2. \tag{5}$$

The maximum alternating current (ac) voltage $V_{\max}$ required is then determined by the maximum mass $m_{\max}$ (in amu) as

$$V_{\max}=14.46\times10^{-8}m_{\max}f^2r_0^2. \tag{6}$$

A conventional quadrupole might be constructed from 5 mm diameter electrodes (so that $r_0=2.177$ mm), with a length of 10 cm. Assuming $m_{\max}\approx 100$ amu, the maximum ac voltage required is $V_{\max}\approx 1.1$ kV at a frequency of 4 MHz. Arranging each electrode pair to act as the capacitive part of a rf resonator typically provides a voltage of this magnitude. Assuming further a minimum axial ion energy of 2 eV, the uncertainty in mass is only $\Delta m\approx 0.05$ amu. However, this high resolution requires a costly, bulky, and fragile insulated mount capable of holding the electrodes accurately parallel at the desired separation.

By reducing the electrode diameter to 0.5 mm, the ac voltage can be reduced to <20 V at a similar frequency. If the electrode length is also reduced by an order of magnitude, the uncertainty in mass exceeds 1 amu; however, a resolution of around 1 amu may be obtained for $L>20$ mm. This suggested that it would be possible to construct a cheap, low-resolution instrument, given a suitable electrode mounting. Because of the reduction in r_e, the precision required exceeds that possible with conventional machining.

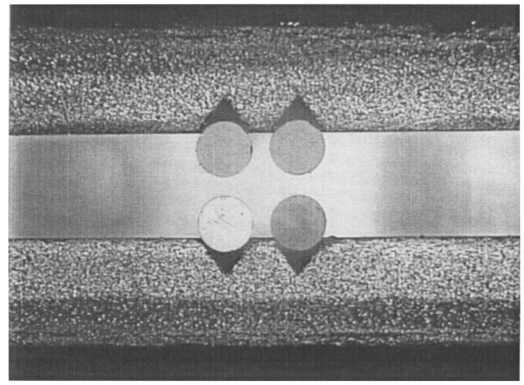

FIG. 1. End on view of the MEMS mass filter. The four QMS electrodes are 0.5 mm diameter, metal coated optical fibers bonded within etched V grooves in two silicon wafers.

A MEMS mass filter was constructed in which four cylindrical electrodes are mounted on silicon substrates as shown in Fig. 1. The correct electrode spacing is achieved through the use of anisotropically etched V grooves as kinematic mounts for both types of rod. Each substrate carries one alignment rod, which mates with a groove on the other substrate. Positional accuracy was achieved by the use of lithography, followed by etching along the crystal planes of the silicon substrate. Provided tangent contacts are made between the rods and the grooves, this construction makes the spacing insensitive to variations in groove width. A simple process for batch fabrication has been developed based on 3 in. diameter ⟨100⟩ p-type silicon wafers and is described in detail elsewhere.[7,8] The electrodes are made from 0.5 mm borosilicate glass, drawn to diameter and metallised using Cr/Au. Using the basic process above approximately 25 mass analyzers have been made, with variant details added as fabrication experience has increased.

B. Radio frequency electronic drive for the MicroQuad

A suitable mechanical assembly was designed to hold and make connections to the microengineered mass filter. This allowed the filter to be assembled in line with a hot filament ion source and electrometer detector, on a conventional vacuum flange to form a MicroQuad QMS as shown in Fig. 2. The initial testing of MicroQuad was carried out using a low power tuned circuit adapted to run at 6 MHz. It was found however, not surprisingly, that the micromachined mass filter operated at these rf represented a low impedance load with significant leakage currents in comparison to a conventional quadrupole mass filter. The electronic drive circuit to the MicroQuad was therefore redesigned using a direct drive technique as opposed to a tuned circuit approach.[9] The incoming control signals indicate to the rf unit what mode to operate in (normal, total ion or beam off) and provide a ''program'' voltage to control the mass position to be analyzed. After buffering and scaling, the program voltage is

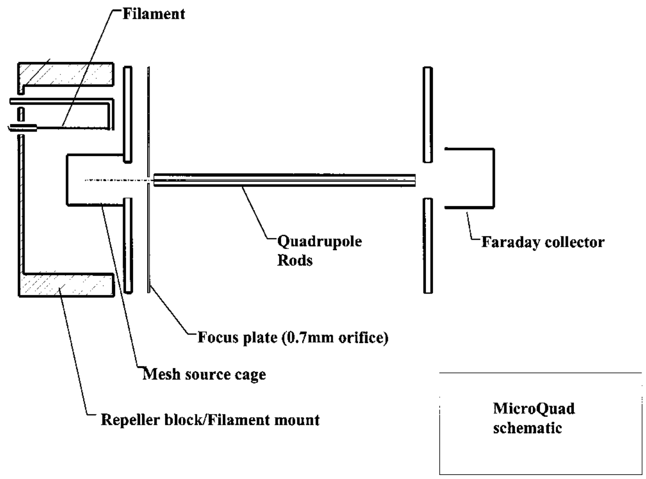

FIG. 2. Schematic diagram of the MEMS mass filter assembled in line with a conventional hot filament ion source and Faraday collector to form the MicroQuad.

passed to a circuit, which generates precise direct current (dc) voltages and also to the oscillator and modulator. The oscillator utilizes a crystal to generate a stable sine wave at 6 MHz. The modulator varies the amplitude of this rf voltage in a precise relationship to the program. Feedback to the modulator is used via a precision active rectifier, to ensure tight control over the absolute voltages being applied to the MicroQuad. The two-phase generator sums the dc and rf voltages and provides a two-phase output.

By introducing the micromachined quadrupole mass filter the ratio of (rf frequency/electrode radius)^2 is reduced by a factor of at least 10. Hence, the maximum rf voltage required in any given application is reduced by the same factor. This allows smaller, simpler and less expensive rf supplies to be used. The high speed and current capability of the output stages eliminates the need for a tuned circuit which normally requires inductors and tuning capacitors to resonate the load. This opens up the possibility of a very compact rf unit being implemented directly in silicon.

III. OPERATION OF THE MICROQUAD

A. Initial results

The first prototype MicroQuad (MkI) was initially tested using a 20 mm long microengineered mass filter, a hot filament ion source with a Faraday collector, and a Keithley Instruments 610 electrometer acting as a detector. By optimizing the operating conditions of the ion source, the mass resolution was steadily increased. Although the proof of quadrupole principle was clearly demonstrated by this result the resolution of the instrument was poor and indeed it was not possible to quantify resolution at 10% peak height.[10]

A second prototype MicroQuad (MkII) was constructed in which a 30 mm micromachined quadrupole mass filter was mounted onto a commercial hot filament ion source, this was in turn attached to a 70 mm vacuum flange. The MEMS fabrication technique for the production of this filter was improved from that used previously by further recessing the earthed silicon ground plane with respect to the rods. This was found by numerical simulation to give a closer approximation to the required hyperbolic field profile for ideal QMS operation.[8] Furthermore for the MkII prototype the improved rf electronic drive unit described earlier in Sec. II B was used. The MkII MicroQuad was tested on two separate occasions separated in time by about three months. The resolution of this instrument was much improved on the MkI version and a linear mass scale with 5%–10% valley separation between O_2/N_2 peaks was obtained. With ion energy of 14 eV the best resolution of the instrument (peak width at 10% peak height) was calculated at 2.7 amu at mass 40.[9]

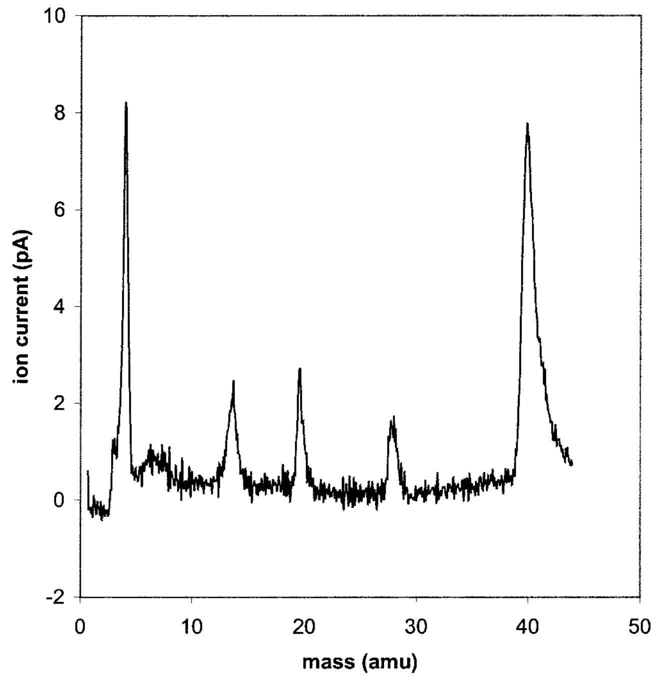

FIG. 3. Mass spectra obtained from the output of the electrometer for an argon/nitrogen/helium gas mixture. Total pressure 2×10^{-5} mbar, ion source voltage 13.5 V, emission current 2 mA, and pole bias 8.7 V.

B. Effect of pole bias

The previous results showed that whilst quadrupole operation was achieved, the low ion current obtained necessitated the use of high ion energies which limited the maximum resolution obtained. A third phase of testing has now been completed using the modified MkII MicroQuad. The instrument operated consistently and in agreement with previously obtained results indicating good instrument stability and reproducibility over a 12 month period. By using a fixed dc bias applied to the electrodes (pole bias) and with careful control of the ion source voltage, an increased ion signal current was obtained. Figure 3 shows MicroQuad spectra for an argon/nitrogen/helium gas mixture. Five peaks are clearly visible corresponding to He^+, N^+, Ar^{2+}, N_2^+, and Ar^+ ions. The signal current (ion transmission) is increased by a factor of 8 over previous best result.[9] The resolution of the QMS was calculated to be about 18 at mass 20 with a peak width of 1.1 amu measured at 10% peak height. The ion source

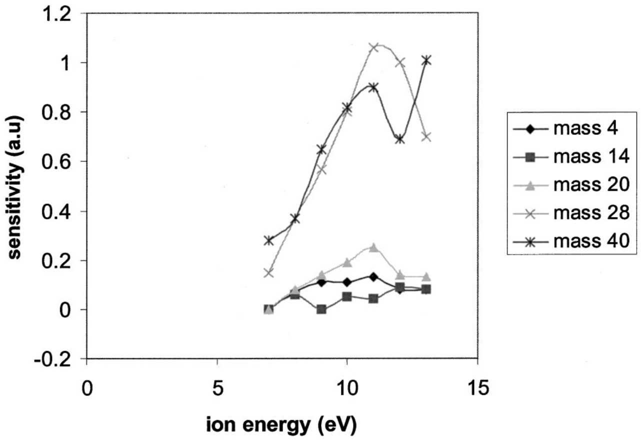

FIG. 4. Effect of ion energy on sensitivity (in arbitrary units) for constant source voltage and varying dc pole bias to the QMS rods.

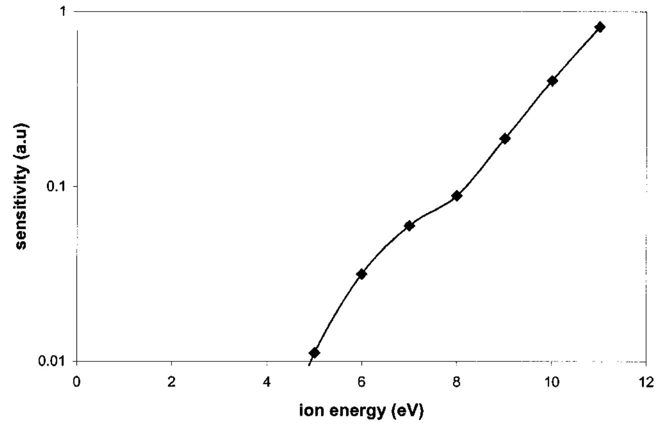

FIG. 6. Sensitivity (in arbitrary units) against ion source voltage for the same conditions and spectra as shown in Fig. 3.

voltage was set at 13.5 V with a pole bias of 8.7 V, the ion source emission current 2 mA, and focus voltage −50 V. The total pressure was 2×10^{-5} mbar. However, it can be seen that the peak shapes obtained from the MicroQuad continue to be nonideal, exhibiting long tails on the high-mass side of the spectra, and similar spectra were obtained previously.[9] Such effects may be due to mechanical deficiencies such as rod end misalignment, etc., and have been identified previously on a larger QMS.[6] The effect of applying positive pole bias is to reduce the energy of ions in the filter thus improving resolution, and at the same time aid collection of ions at the zero biased Faraday detector thus improving sensitivity.

Figure 4 shows ion signal current (sensitivity) collected as a function of ion energy for charge to mass (m/e) ratios in the range 4–40. Increased ion current with ion energy was obtained for all ions with the effect being least marked in the case of the singly charged nitrogen ion (mass=14). For the same energy ions with greater m/e ratios will be moving more slowly through the quadrupole leading to improved ion collection at the Faraday detector.

Figure 5 shows the effect on the peak width of reducing the ion energy below 10 eV for a range of singly charged argon ion spectra (mass=40). Figure 6 shows the corresponding effect on ion transmission (sensitivity) for the same spectra. Resolution is much improved low ion energies but at the expense of reduced signal. Sensitivity increases exponentially with ion energy over the range considered. This is probably due to ions with low energy from the hot filament ion source having poor entrance efficiency into the MicroQuad mass filter. Work is ongoing to address this problem via fabrication of a miniature ion source to couple directly to the filter. Figure 7 shows the resulting performance curve from Figs. 3 and 4 for the MicroQuad at mass 40 obtained by varying the U/V voltage ratio whilst keeping the ion energy at approximately 2 eV and other parameters constant. The curve shows the typical trade-off of sensitivity against resolution obtained for conventional quadrupole mass filters. There is a gain in resolution by a factor of 4 for a 20 fold reduction in sensitivity with a minimum peak width of 1.3 amu at mass 40, corresponding to a best case resolution of 31.

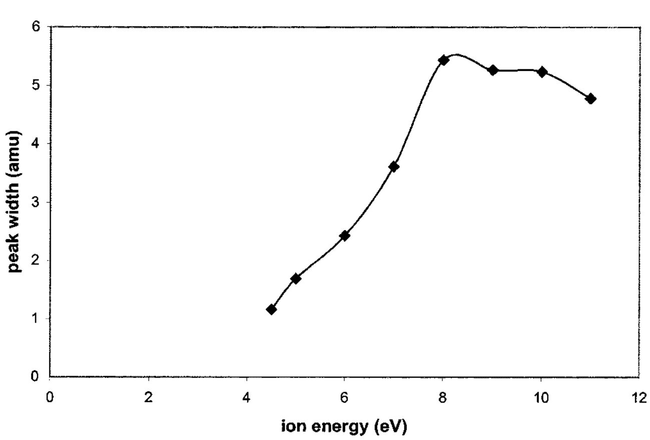

FIG. 5. Peak width at 10% peak height against ion source voltage (ion energy) for a range of argon spectra. Emission current 0.2 mA and pressure 5×10^{-5} mbar.

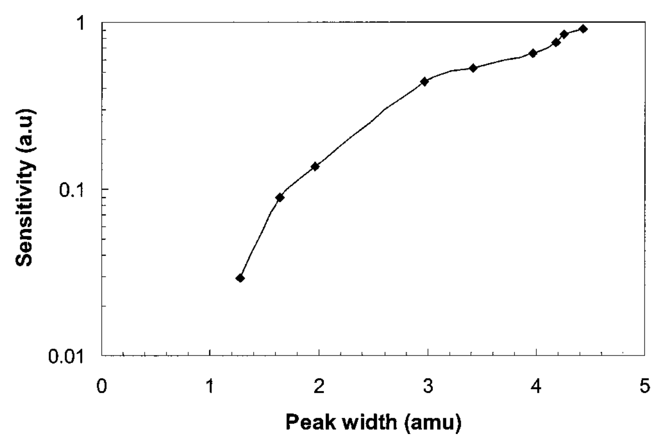

FIG. 7. Sensitivity (in arbitrary units) against peak width at 10% peak height for varying U/V voltage ratios for the same conditions and spectra as shown in Fig. 3. Ion source voltage 8.7 V, pole bias 7 V, ion source emission current 0.2 mA, and pressure 3×10^{-5} mbar.

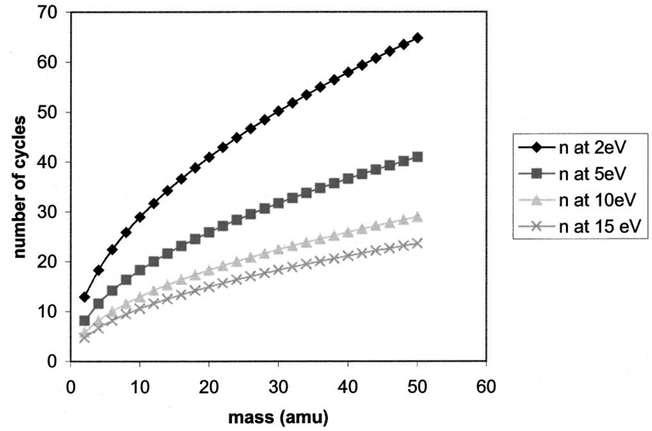

FIG. 8. Predicted number of rf cycles experienced by the ions in the MicroQuad mass filter of length 30 mm and rf 6 MHz as a function of m/e for different ion energies.

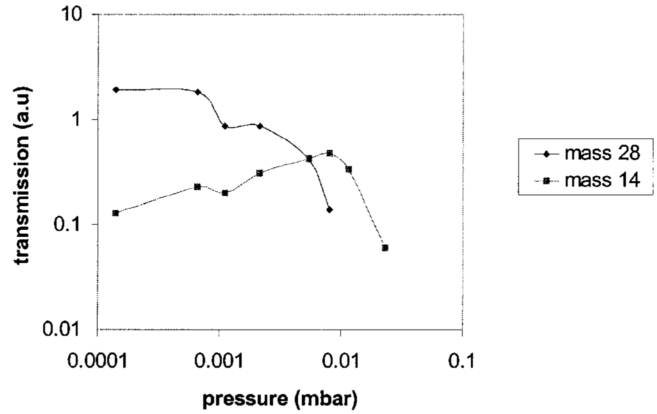

FIG. 10. Transmission (in arbitrary units) against pressure for nitrogen spectra in the pressure range to 10^{-1} mbar and ion source emission current 0.2 mA.

By applying Eq. (3) the number of rf cycles n experienced by the ions entering the MicroQuad mass filter for different ion energies may be calculated and is shown in Fig. 8. For ions of mass 40 entering the filter with 2 eV energy, the number of cycles n is approximately 60, corresponding to a predicted resolution of 180 by Eq. (4), with resolution ($m/\Delta m$) quantified at 10% peak height. For ions of mass 40 entering the filter with 5 eV energy, the number of cycles n is approximately 36, corresponding to a predicted resolution of 65. Predicted resolution is therefore much lower than that obtained in practice (Figs. 3 and 7) by a factor of between 5 and 6. One reason for this is due to the nonideal peak shapes. The high-mass tails on the spectra give a large value of Δm at 10% peak height. Clearly the MicroQuad resolution could be considerably improved if this were not the case.

C. MicroQuad operation at high pressures

Figure 9 shows the peak heights for N_2^+ and N^+ ions in pressure range 10^{-6}–10^{-3} mbar. The pressure was measured using a MKS Baratron pressure gauge. The N_2^+/N^+ ratio increases with pressure over the range with the larger signal corresponding to increased ionization and transmission for $m/e = 28$ ion as the pressure increases. This effect is probably due to its greater ionization cross section of N_2^+, but may be due to space charge effects in the ion source. Figure 10 shows the same nitrogen spectra in the pressure range up to 2.5×10^{-2} mbar. Transmission of the mass 28 ion reduces with pressure in the pressure range above 10^{-3} mbar, whereas transmission of the mass 14 continues to increase up to 10^{-2} mbar. The falloff of transmission with increasing pressure is probably due to increased probability of ion-neutral collision over the path length of the mass filter. For the larger mass ion the falloff is greater due to the larger collision cross section. It can be seen, however, that although the signal is reduced the MicroQuad remains useable into this pressure regime and this is a feature of the small size of the instrument. Some miniature quadrupole gas analyzers use a correction factor to compensate for ion collision with neutral gas molecules in the mass filter and thus allow instrument use at higher pressures.[11]

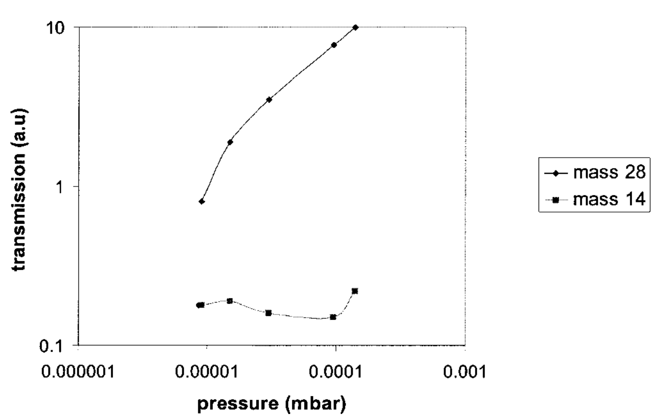

FIG. 9. Transmission (in arbitrary units) against pressure for nitrogen spectra in the pressure range to 10^{-3} mbar and ion source emission current 0.5 mA.

IV. CONCLUSIONS

Stable and reproducible quadrupole operation for a silicon based QMS with a fully micromachined mass filter operating at low power and low voltages has been demonstrated. The MicroQuad mass filter behaves as a conventional mass lens with a typical tradeoff between ion transmission (sensitivity) and resolution. For the MEMS mass filter studied here the resolution (at 10% peak height) was found to vary approximately as $1/\sqrt{S}$ (where S=sensitivity) with a best case resolution of 31 (at mass 40). Performance improvement over initial prototypes is felt to be due to (i) improved design of the micromachined filter, (ii) the use of a direct rf driving electronics as opposed to a tuned circuit, and (iii) the reduction of ion energy afforded by the pole bias applied to the mass filter. Application of the pole bias results in improved ion collection and increase instrument sensitivity, however, the best case resolution of 31 obtained to date is much lower than that predicted by simple theory and is probably a consequence of nonideal peak shapes. Such peak shapes may be caused by the inefficient coupling of ions into the mass filter causing transmission of spurious high m/e ions and this issue remains the subject of further investigations. One of the advantages of a miniature mass spectrometer is the ability to operate at higher pressures and we find that for nitrogen ions the MicroQuad operates with increasing signal up to about 10^{-2} mbar and remains operable up to 2.5×10^{-2} mbar, howbeit, with reduced sensitivity.

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