Microfabricated Quadrupole Ion Trap for Mass Spectrometer Applications

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An array of miniaturized cylindrical quadrupole ion traps, with a radius of 20 μm, is fabricated using silicon micromachining using phosphorus doped polysilicon and silicon dioxide for the purpose of creating a mass spectrometer on a chip. We have operated the array for mass-selective ion ejection and mass analysis using Xe ions at a pressure of 10^{-4} Torr. The scaling rules for the ion trap in relation to operating pressure, voltage, and frequency are examined.

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The quadrupole ion trap was invented by Wolfgang Paul during the 1950s with the goal of creating a trap for the purpose of studying isolated particles in a confined and controlled environment [1,2]. The instrument has since been researched, developed, and commercialized extensively with applications in many areas of biology, chemistry, geology, and physics. One embodiment of the ion trap is the quadrupole ion trap mass spectrometer (QITMS), which is used for quantitative gas analysis, isotope determination, and detection of trace pollutants and drugs. The usage of a gas chromatograph and mass spectrometer (GC-MS) combination is considered to be the ‘‘gold standard’’ of chemical analysis and detection of volatile organic species. While such an accurate and sensitive instrument exists in bulky form in many analytical laboratories, there is a high demand for a smaller and more portable version of the chemical sensor for remote and widespread deployment. This demand has stimulated researchers to seek ways to miniaturize and mass produce a GC-MS system. The holy grail is the development of a mass spectrometer on a chip that has the same mass range, sensitivity and resolution as existing systems, but with smaller size, operating voltage, and power consumption. We report here a significant step in achieving this goal by demonstrating the usage of a 20 μm radius microfabricated ion trap array to perform mass spectrometry of Xe ions at the operating pressure of 10^{-4} Torr.

The quadrupole ion trap is particularly conducive to scaling and implementation by existing microfabrication technology. A quadrupole potential can be generated by using three electrodes in a cylindrical geometry [3–7]. The top and bottom electrodes are usually grounded in the mass-selective instability operation mode and the middle ring electrode is driven by an rf voltage of frequency Ω [2]. The largest mass that can be ejected by ramping the rf voltage [2] and the mass resolution [8] are given by

$$\left(\frac{m}{e}\right)_{\max} = \frac{8V_{\max}}{q_{\max}\Omega^2(r_0^2 + 2z_0^2)}, \quad (1)$$

and

$$\frac{\Delta m}{m} \propto \frac{2\sqrt{3}c}{\Omega} = \frac{4\sqrt{3}}{\Omega\tau}, \quad (2)$$

respectively, where e is the charge, m is the ion mass, $V_{\max}$ is the voltage amplitude on the middle ring electrode, $q_{\max} = 0.908$ is a constant, r_0 is the radial dimension of the trap, z_0 is the height dimension of the trap, and c is a drag coefficient associated with the ambient gas, equal to $2/\tau$. The quantity τ is the collisional relaxation time [9], inversely proportional to the buffer gas pressure. We note that in shrinking the trap dimensions, r_0 and z_0, it is possible to maintain a constant mass range and resolution by changing the operating voltage, frequency, and pressure.

Two areas of increasing research in mass spectrometry are focused on making smaller quadrupole ion traps and operation at higher pressure [8,10]. In the former case, the intention is to create massive arrays of quadrupole ion traps on a chip that provide a higher signal-to-noise ratio, utilize a smaller amount of analyte, require lower power consumption, and occupy a smaller form factor. The advantage of high-pressure operation is the elimination of the turbo pump and the overhead associated with high vacuum mechanical pumping. Higher pressure can also increase sample concentration in the ionization region and has been shown to increase sensitivity in ion mobility spectrometry [11]. From space charge considerations, the number of ions that can reside in a single trap is proportional to the radius of the trap, $N_{\max} \propto r_0$ [12]. In an area with one trap of radius r_0, it is possible to replace the single trap with an array of n smaller traps with radius r_s, such that $r_s = r_0/\sqrt{n}$. Thus, by using an array of small traps, one can potentially gain a factor of $\sqrt{n}$ in the number of trapped ions, for the same area, if the same trap energy depth is maintained.

The requirements to reduce trap size and to operate at high pressure are not independent. As the trap size decreases, the ion orbit inside the trap is also reduced because the quadrupole electric field increases. From Eq. (2), the operating frequency Ω should be increased proportional to the pressure to maintain mass resolution. From Eq. (1), the

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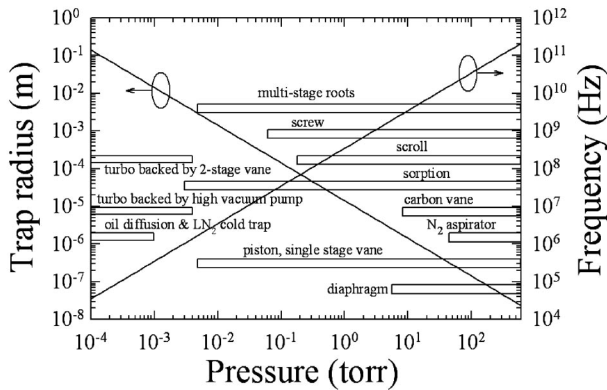

FIG. 1. Projected scaling characteristics of a quadrupole ion trap. The radius of the ion trap, r_0, and operating frequency, Ω, are plotted as a function of operating pressure for $m = 100$ amu, $\Delta m = 1$ amu, $V = 100$ V, and $q_z = 0.4$. The performance ranges of different pumps are also shown [13].

trap dimensions must then be reduced to maintain mass range. Thus, miniaturization of the ion trap actually enables high-pressure mass spectrometry. Figure 1 shows the projected relationships between trap dimension, driving voltage frequency, and operating pressure based on these ideas. The operating pressure of different types of vacuum pumps are also shown [13]. In general, we see two important trends: as the pressure is increased, the operating frequency must increase and the dimensions decrease if the same voltage is applied. At a trap radius of 20 μm, the maximum operating pressure should be greater than 1 Torr, which can be generated by existing microelectromechanical system (MEMS) pumps. The prospect of integrating the ionization source, ion trap, ion sensor, and vacuum pump on the same substrate and in a small form factor becomes feasible in this respect. We will demonstrate that such a microfabricated array of ion traps can function at this dimension.

The original quadrupole ion trap was made of electrodes of hyperbolic shape [2]. Alternative geometries have been explored in attempts to simplify the electrodes construction. The cylindrical ion trap (CIT) has a simple geometry that can be machined and microfabricated and has been shown to yield mass spectra with subunit mass resolution [14]. Experimental results have shown that the optimal quadrupole potential can be achieved for dimensions $z_0 \approx r_0$, where z_0 and r_0 are the half height and radius of the cylinder [3]. We have successfully fabricated an array of CITs with $r_0 = 20$ μm using p-doped polysilicon as electrodes and silicon dioxide as insulating layers. Figure 2 shows the dimensions and geometry of the microfabricated

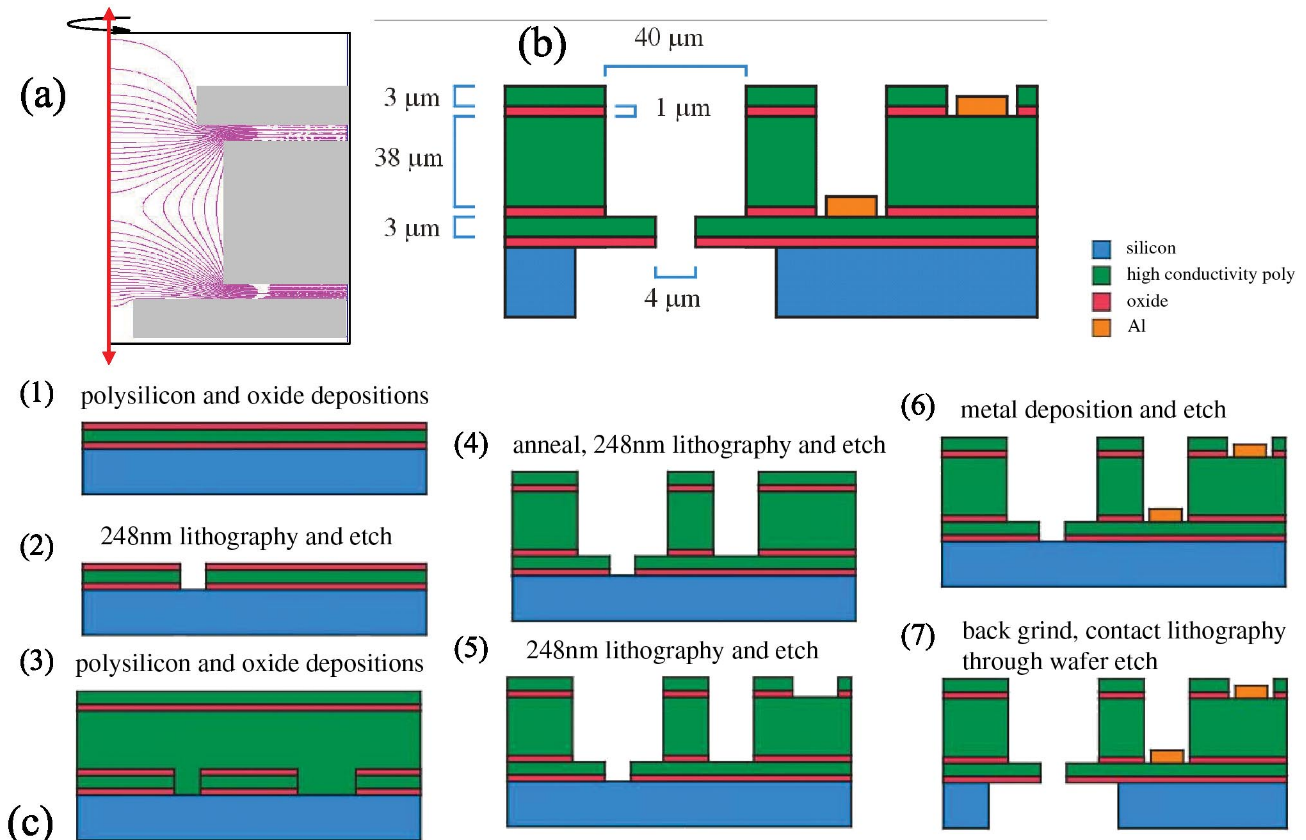

FIG. 2 (color). Design and fabrication of ion trap array. (a) Diagram of an open cap cylindrical ion trap and equal potential field lines calculated using SUPERFISH [17]. (b) The dimension of the ion trap. (c) Schematic of the fabrication process.

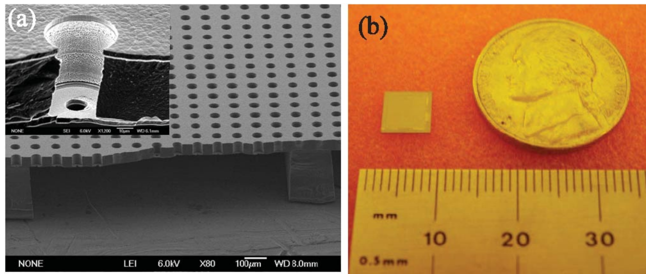

FIG. 3 (color). Microfabricated ion trap. (a) Scanning electron micrograph and (b) picture of ion trap chip showing the dimensions of the structure.

ion trap and the array chip. The CIT has an open end cap structure. The fabrication process requires six lithographic and etching steps, five on the front and one on the back side of an 8 in silicon wafer. The choice of phosphorus doped polysilicon with resistivity of $\rho \leq 10^{-3}$ Ω cm as our conducting material allows us to create structures that are over 40 μm thick. There are advantages and limitations to the usage of polysilicon electrodes. Polysilicon can be deposited with high precision to thickness up to 100 μm. It can be doped to have low resistivity ($<10^{-4}$ Ω cm) and patterned in high aspect ratio ($>$1:20), uniformity ($>$95%), and smooth side walls ($<$10 nm). There is presently no simple way to deposit and to etch such a thick layer ($>$1 μm) of metal using conventional integrated circuit fabrication techniques [15]. High conductivity is desirable for low rf loss. On the other hand, polysilicon electrodes cannot be directly wire bonded and additional metallization is necessary to make contact to the silicon. The polysilicon is deposited by chemical vapor deposition and is subsequently annealed at 1050 °C for 10 hours to relieve any residual stress. Patterning of the thick polysilicon is done using the standard deep reactive ion etch process. Care must be taken to create a smooth sidewall to minimize any fluctuating potential that can heat the ions. The final device is a membrane structure with an opening on both sides of the membrane for entrance and exit of ions. Stress engineering is extremely important in such a membrane structure in order to prevent cracks and delaminations. We have performed more than five iterations of design and processing over the past two years before arriving at the current functional device. Images of the trap cross section and chip are shown in Fig. 3. The scanning electron micrograph shows the three ring electrodes separated by a thin and recessed oxide layer. The thickness of the insulating layer is thick enough to prevent breakdown and thin enough to prevent disturbance of the trapped ion from the charging of the dielectric oxide. From our experience, we found that it is important to minimize the exposure of the ions to any insulating dielectric, which can harbor localized surface charges and create time varying parasitic potentials.

The experimental setup is shown in Fig. 4(a). The vacuum chamber is filled with approximately 1% Xe gas and 99% He gas at a pressure of 10^{-4} Torr. The tungsten filament is biased at -70 V and heated by a current of 2.2 A to generate electrons to ionize the ambient Xe. During ejection, the gate shutter is biased at -120 V to turn off the beam of electrons. The mesh is biased at -600 V to accelerate Xe ions ejected from the trap. The ions are detected with a channel electron multiplier biased at -1200 to -1600 V. The multiplier has a gain of approximately 10^6 at the maximum bias voltage. We tested array samples of 256 and 2304 traps. Impedance matching

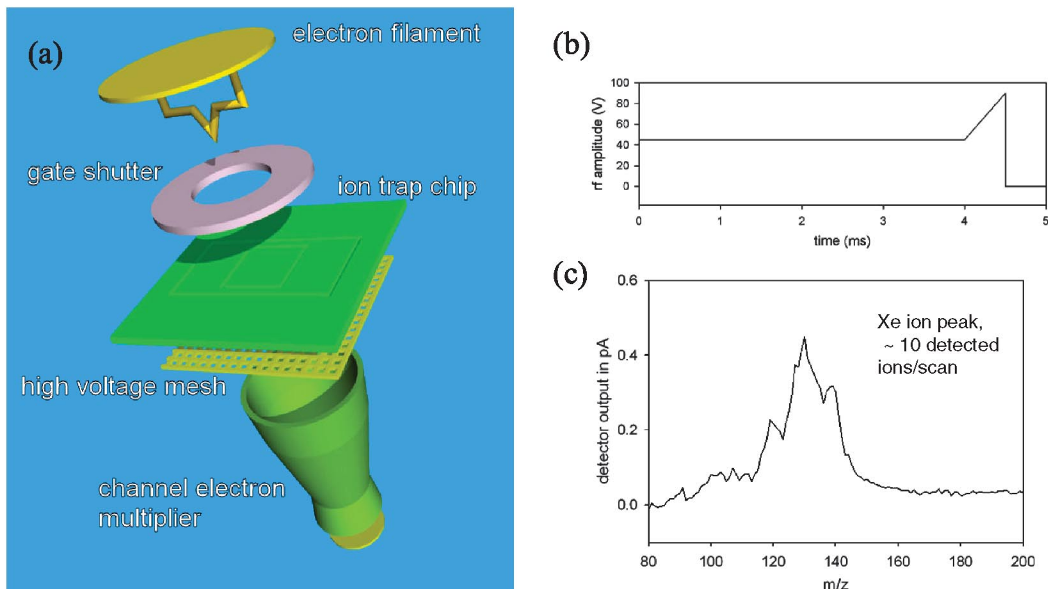

FIG. 4 (color). Experimental results. (a) Diagram of experimental setup. (b) Scan function showing electron gun on during 0 to 4 ms and detector turn-on during 4 to 5 ms. (c) Ion signal (Xe) obtained at a He pressure of 10^{-4} Torr. Origin is located at 4.09 ms.

of the chip to the driving electronics is an important issue and we found that we could apply a higher voltage (larger trapping potential) to the smaller array of traps because the chip has a smaller active area and a lower capacitance. Figures 4(b) and 4(c) shows the timing diagram and the mass spectra of the Xe ions taken using the 256 trap array. The rf electrode was driven at 100 MHz with an amplitude of 45 V during trapping and ramped from 45 to 90 V in 200 μs for the mass scan. We estimate that the observed signal corresponds to approximately ten ions per scan.

The development of the microfabricated quadrupole ion trap has enabled the miniaturization of the mass spectrometer. In addition to chemical sensing, the ion trap technology has applications in quantum computing, MEMS dipole and ion pump, ion generation, atomic clock, and precision spectroscopy. While we have demonstrated the operation of a 20 μm ion trap array, we are currently limited by the availability of ion detection and amplification at high pressure. Electron multipliers can operate at a pressure of 10^{-4} Torr but suffer from electrical breakdown at higher pressure. One avenue of future investigation is to develop a high-pressure ion amplifying detector, either using chemical amplification or electron-to-photon conversion followed by subsequent photon amplification and detection. Another avenue of future investigation is to continue shrinking the size of the ion trap, such that there is enough ion signal generated to be detected by a Faraday cup or an array of microfabricated Faraday cups [16]. Current fabrication techniques allow us to precisely create structures below 100 nm. How small can we make an ion trap before it stops working? For an operating pressure of 76 Torr (0.1 atm), the size of the ion trap has to be reduced to about a micrometer. The operating frequency would be in the GHz range, and matching the driving electronics and device impedance becomes more difficult. In order to trap ions, the trap potential must be greater than the thermal energy. The pseudopotential well depth along the radial direction, D_r, is given by

$$D_r = \frac{eV^2}{4mr_0^2\Omega^2} = \frac{Vq_r}{8} \geq \frac{k_B T}{e}, \tag{3}$$

where $0 \leq q_r \leq 0.908$ is the radial Mathieu parameter. As we reduce the size of the trap, we must increase the operating frequency and decrease the operating voltage to maintain the trapping condition. Equation (3) gives a lower bound for V. Of course, this restriction can be circumvented by cooling the ions using additional overhead such as laser cooling or sympathetic cooling. In principle, there is no limit on the frequency Ω, since we can always design the ion trap to occupy the antinodal position of a transmission line. In practice, it is not clear how the trap will scale to below 100 nm, where the roughness of the electrode from fabrication becomes sizable and the operating frequency goes above 10 GHz. Depending on the type of etching chemistry, the side wall roughness can range from 1–10 nm. The presence of a random and rapidly fluctuating potential is likely to heat the ions, ejecting them from the trap, and adding noise to the mass spectrometry signal. Thus, there exists a practical limit to the size of the scaling and this limit is determined by existing fabrication technologies.

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[1] W. Paul, Rev. Mod. Phys. **62**, 531 (1990).
[2] R. E. March and J. F. J. Todd, *Practical Aspects of Ion Trap Mass Spectrometry* (CRC, Boca Raton, 1995), Vol. 1.
[3] E. R. Badman and R. G. Cooks, J. Mass Spectrom. **35**, 659 (2000).
[4] S. Pau, Appl. Phys. Lett. **87**, 134104 (2005); C. S. Pai, S. Pau, and J. A. Taylor, Mass Spectrometers on Wafer-Substrates, U.S. Patent No. 6967326.
[5] R. G. Brewer, R. G. DeVoe, and R. Kallenbach, Phys. Rev. A **46**, R6781 (1992).
[6] J. M. Wells, E. R. Badman, and R. G. Cooks, Anal. Chem. **70**, 438 (1998).
[7] M. G. Blain, L. S. Riter, D. Cruz, D. E. Austin, G. Wu, W. R. Plass, and R. G. Cooks, Int. J. Mass Spectrom. **236**, 91 (2004).
[8] W. B. Whitten, P. T. A. Reilly, and J. M. Ramsey, Rapid Commun. Mass Spectrom. **18**, 1749 (2004).
[9] D. E. Goeringer, W. B. Whitten, J. M. Ramsey, S. A. McLuckey, and G. L. Glish, Anal. Chem. **64**, 1434 (1992).
[10] R. J. Ferran and S. Boumsellek, J. Vac. Sci. Technol. A **14**, 1258 (1996).
[11] G. A. Eiceman and Z. Karpas, *Ion Mobility Spectrometry* (CRC, Boca Raton, 1994).
[12] H. G. Dehmelt, Dv. Atom. Mol. Phys. **3**, 53 (1967).
[13] J. F. O'Hanlon, *A User's Guide to Vacuum Technology* (Wiley, New York, 2003), 3rd ed.
[14] J. Moxom, P. T. A. Reilly, W. B. Whitten, and J. M. Ramsey, Rapid Commun. Mass Spectrom. **16**, 755 (2002).
[15] On the other hand, for ion trap of dimensions of the order of 1 μm, metals such as aluminum, titanium, titanium nitride or tungsten, which are compatible with integrated circuit fabrication, can be used as electrode instead of doped polysilicon.
[16] A. A. Scheidemann, R. B. Darling, F. J. Schumacher, and A. Isakharov, J. Vac. Sci. Technol. A **20**, 597 (2002).
[17] Los Alamos Accelerator code Group, *Poisson/SUPERFISH Reference Manual*, LA-UR-87-126 (Los Alamos National Laboratory, Los Alamos, NM,1987).