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TRENDS

Advances in microfabricated mass spectrometers

R. R. A. Syms

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Abstract Mass filters for miniature mass spectrometers are now being constructed using three-dimensional microfabrication techniques. Crossed-field, travelling-wave, time-of-flight, quadrupole and cylindrical ion-trap filters have all been demonstrated, with steadily increasing mass range and mass resolution. This paper reviews the range of available devices and the state of the art.

Keywords Mass spectrometer · Mass filter · Microelectromechanical systems

Introduction

Over the past century, mass spectrometers have evolved into exceptional analytical instruments. Many ways to separate ions were investigated, mass range and resolution were raised considerably, and analytical power increased by fragmentation of selected ions. Mass spectrometry was combined with gas and liquid chromatography and capillary electrophoresis, and electrospray and matrix-assisted laser desorption ionisation were used to investigate complex biomolecules. However, instruments remain bulky and expensive, and until recently a 'personal' mass spectrometer was a dream. Now the situation may be changing. Much of the bulk is due to the pumping system. If the mass filter can be shrunk without severely degrading sensitivity, the mean free path reduces, lowering pumping requirements. Filters are multielectrode assemblies with many precision components; if these can be manufactured using integrated processes that retain accuracy at a small size scale, assembly costs can be reduced. The concept is therefore emerging of a low-cost benchtop system based on a microfabricated filter with moderate sensitivity, mass range and resolution.

Many miniature filters have been constructed at the limit of conventional machining; however, until recently the performance of microfabricated filters has been inadequate. After a slow start in the 1990s, confidence in this approach is now increasing. However, the key new enabler is microelectromechanical systems (MEMS) technology, a method of forming complex structures using planar microfabrication steps such as photolithography, deep reactive ion etching and metallisation, often on silicon substrates.

R. R. A. Syms (✉)
EEE Department, Imperial College London,
Exhibition Road,
London SW7 2AZ, UK
e-mail: r.syms@imperial.ac.uk

Development of microfabricated filters

MEMS mass spectrometers have been successfully developed as Wien filters, travelling-wave and time-of-flight (TOF) filters, quadrupole filters and ion traps. Each type presents different challenges. Advances have generally been made when new methods of constructing the 3D geometries needed in ion optical systems or overcoming the poor mechanical and electrical properties of silicon have been found.

The first credible microfabricated mass spectrometer was a Wien filter mass spectrograph constructed by Freidhoff [1]. The device is based on a continuous ion source, fixed, crossed magnetic and electric fields, and a detector array. The whole analyser except for the ion source is formed in a shallow cavity etched into a silicon substrate a few centimetres long (Fig. 1a). The key difficulty overcome was to provide an in-plane transverse electric field using an electrode array, despite the presence of nearby grounded magnet poles. A mass range of 200 atomic mass units (amu) and a resolution of 150 amu were achieved.

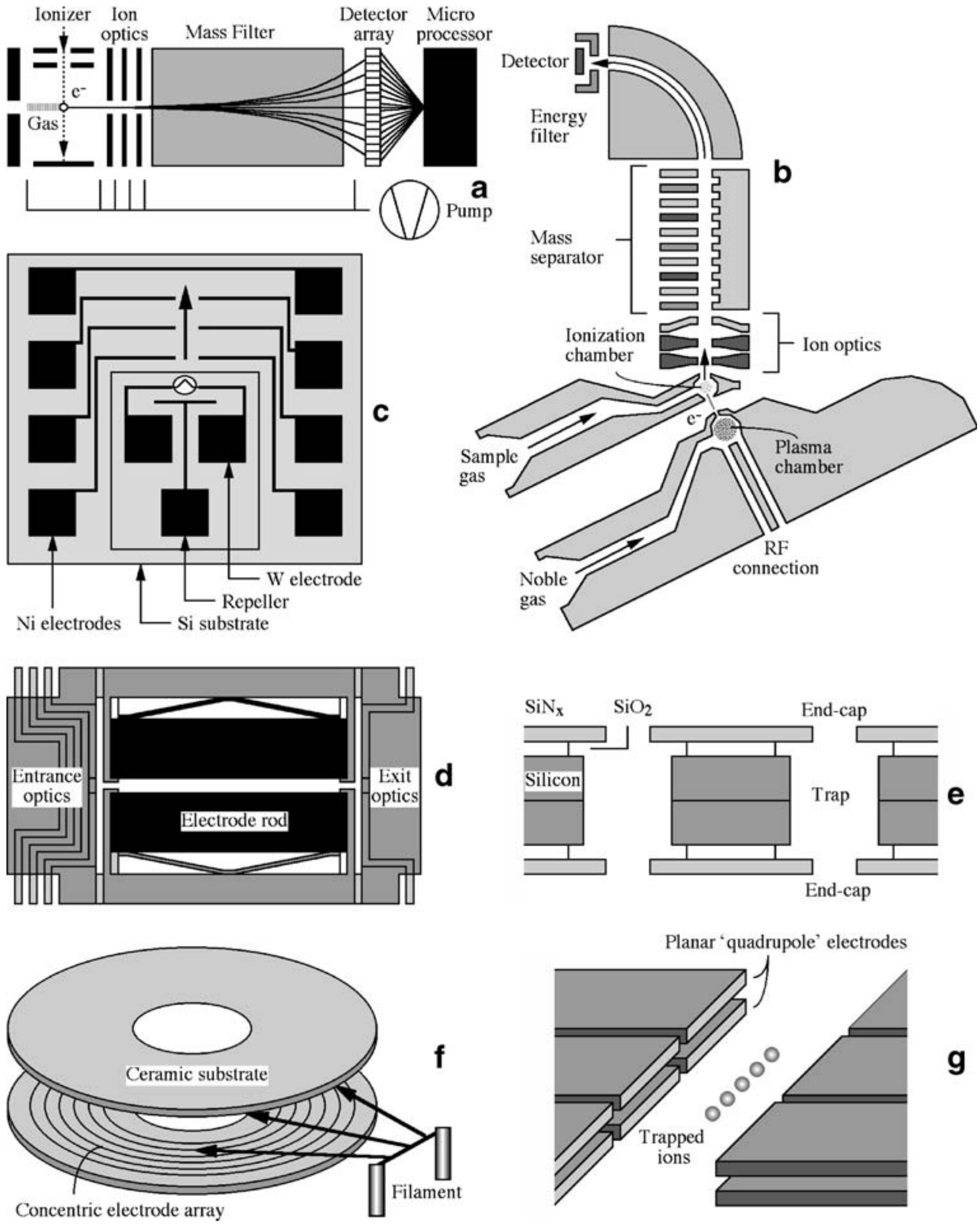

Fig. 1 Microfabricated mass filters: **a** crossed-field [1], **b** travelling-wave [2], **c** time-of-flight [3], **d** quadrupole [7], **e** cylindrical trap [13], **f** halo trap [15], **g** linear trap [16]

Because magnetic separators do not scale well into the microstructure size domain, the majority of microfabricated filters have performed separation by time-varying electric fields. For example, Hauschild et al. [2] have constructed a planar integrated micro mass spectrometer (PIMMS), which uses an electrostatic sector as an energy filter and a travelling-wave electric field generated by a periodic electrode array to separate ions. The entire structure is fabricated as a single chip measuring 5 mm×10 mm on a silicon-on-glass wafer (Fig. 1b), which is sealed with a second glass wafer to form an integrated vacuum chamber operating at 1-Pa pressure. Argon plasma at 50 Pa provides a source of electrons for ionisation. A mass range of 80 amu and a mass resolution of approximately 5 amu were achieved.

For microfabricated TOF filters, the challenge is to achieve sufficient separation in a short path. The first MEMS TOF mass spectrometer was constructed by Yoon et al. [3], who used a silicon substrate with plated electrodes in the classic Wiley–McLaren geometry (Fig. 1c). Although a suspended tungsten filament was incorporated, spectra were only obtained with a pulsed laser source. Wapelhorst et al. [4] have also demonstrated a TOF version of the PIMMS, replacing the travelling-wave filter by a drift section. A mass range of 50 amu and a resolution of approximately 5 amu were achieved. A reflectron TOF instrument based on a plug-assembled 3D silicon electrode stack is under construction by Verbeck et al. [5].

For microfabricated quadrupole filters, the challenge is to devise precise methods of mounting cylindrical electrodes.

MEMS quadrupoles were first constructed by Syms et al. [6], using two grooved silicon wafers separated with spacers to seat pairs of metallised glass rods. The mass range was limited to 100 amu by RF heating due to capacitative coupling through the substrate, which increases rapidly with voltage. A more recent design with integrated coupling optics used springs etched in bonded silicon material to retain 30-mm-long, 0.5-mm-diameter stainless steel electrodes (Fig. 1d) and achieved a mass range of 400 amu and a resolution of 2 amu at 6-MHz frequency [7]. This filter has been used in battery-powered portable and benchtop mass spectrometers, each with sample introduction by solid-phase microextraction [8]. An out-of-plane quadrupole using spring mounts has also been constructed by Velasquez-Garcia and Akinwande [9].

For microfabricated quadrupole ion traps, the difficulty is to fabricate hyperbolic electrodes. Efforts have concentrated on the cylindrical electrode approximation, which is simpler to construct, and can be formed as a 2D array to overcome space charge limitations on ion storage. Following work on miniature stainless steel traps by Wells et al. [10] and Kornienko et al. [11], cylindrical traps have been constructed in polysilicon by Pau et al. [12], and deep reactive ion etched silicon (Fig. 1e) by van Amerom et al. [13]. Blain et al. [14] have fabricated an array of 10^6 cylindrical traps with an internal radius of 1 μm using chemical vapour deposition of tungsten on silicon. Here, the aim of the large array was to increase signal from a device constructed using a given layer thickness. There has also been interest in planar electrode approximations to hyperbolic geometries. A toroidal, or "halo", ion trap, which has greater storage capacity than a cylindrical trap, has been constructed using concentric electrodes on two stacked wafers (Fig. 1f) by Austin et al. [15], and a linear ion trap based on three sections of planar "quadrupole" electrodes (Fig. 1g) has been proposed by Madsen et al. [16].

Outlook

New methods of microstructuring that allow 3D electrodes to be formed in high-performance materials with accurate and desirable geometries are now allowing microfabricated mass filters to be made with increasingly realistic performance. Challenges still remain in increasing mass range, mass resolution and ion throughput and in developing methods of coupling to atmospheric-pressure ionisation sources. However, it appears only a matter of time before microfabricated devices start providing alternatives to conventional systems.

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