A Fully Micro-fabricated Planar Array of Electrospray Emitters for Space-propulsion Applications

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Sponsorship: AFOSR, DARPA

Electrospray thrusters work by extracting ions or charged droplets directly from a liquid surface using an electrostatic field and accelerating them in that field to produce thrust [1]. This method could lead to more efficient and precise thrusters for space propulsion applications. Emission occurs from sharp emitter tips, which enhance the electric field and constrain the emission location. The electrospray process limits the thrust from a single tip. To get into the millinewton range will require an array with tens of thousands of emitters. Batch microfabrication is well suited to making this array.

We have designed, built, and tested a thruster made in silicon using deep reactive ion etching (DRIE) and wafer-bonding technology (see Figure 1). This thruster comprises two components. The emitter die has up to 517 emitters in a 0.75 cm\(^2\) area, formed using DRIE and SF\(_6\) etching, and is plasma treated so that liquid can be transported to the tips in a porous black silicon surface layer. The extractor die incorporates the extractor electrode, a Pyrex layer for insulation, and the springs, which are used to reversibly clamp the emitter die [2]. This versatile assembly method allows the extractor die to be reused with multiple emitter dies and potentially with emitter concepts radically different from the one we have experimented with.

Figure 2 shows data collected when firing the thruster with the ionic liquid EMI-BF\(_4\). Measurable emissions occurred for extraction voltages down to 700 V. The current collected on the extractor electrode was less than 3% of the emitted current over a wide operating range and often less than 0.1%. Beam-divergence half-angles were between 15 and 30 degrees, depending on the operating conditions. Emitted currents of 500 nA/emitter were observed in stable operation, for expected thrusts of 25 nN/emitter. Time-of-flight measurements prove operation in the ion emission regime, which is most efficient for propulsion.

**Figure 1:** The assembly mechanism (top-left), the extractor electrodes (top-right), diagram of the thruster (bottom).

**Figure 2:** Time of flight data (top) and current-voltage characteristic (bottom) of the thruster.

**REFERENCES**


Low-power, low-voltage, efficient field emission neutralizers for FEEP [1], colloid thrusters [2], and other micro-propulsion engines are attractive for nanosatellites because they do not use mass flowrate to operate, unlike more conventional neutralizing solutions such as hollow cathodes [3]. Electrons are field-emitted from the surface of metals and semiconductors by the application of a high electrostatic field. Field emitters use high aspect ratio structures to generate very high fields even when low voltages are applied. The ideal field enhancing structure is a rounded whisker [4]. Micro-engineered field emission neutralizers would have smaller starting voltages, better area usage, and more uniform I–V characteristics, compared to macro/meso fabricated field emitter versions. Plasma-Enhanced Chemical Vapor Deposited (PECVD) Carbon Nanotubes (CNTs) are rounded whiskers with 100 nm or less of tip radius and 13 µm or more tall. The adoption of CNTs as electron-emitting substrate has recently being shown to have advantages compared to Spindt emitters because of the higher aspect ratio of CNTs and their superior resistance to harsh environments. This research focuses on the development of a batch-fabricated MEMS neutralizer that uses PECVD CNTs as field enhancers (Figure 1). As a reference, a previously made Busek-MIT MEMS CNT device that uses a randomly oriented CNT matrix produced by Busek Co. (Natick MA) with a proprietary arc-based process yielded devices with Fowler-Nordheim emission, startup voltage as low as 100 V, and electron currents as large as 3.2 mA/cm² with about 20% of gate current interception.

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**References**


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▲ Figure 1: Top view of a 14-µm-tall CNF forest inside a microfabricated well. The well has integrated a gate to bias voltage to the CNT forest to produce field emission.

▲ Figure 2: The I-V characterization of a similar CNT-based field emitter array. The device was jointly developed with the Busek company (Natick, MA)
A High-density Electron Source that Uses Un-gated Transistors for Ballasting

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Sponsorship: AFRL

Electrons are field emitted from the surface of metals and semiconductors when the potential barrier (work function) that holds electrons within the metal or semiconductor is deformed by the application of a high electrostatic field. Field emitters use high aspect ratio structures with tips that have nanometer dimensions to produce a high electrostatic field with a low applied voltage. We are implementing two types of field enhancers: carbon nanofibers (CNFs) and silicon conical tips (Figure 1). Spatial variation of tip radius results in the spatial variation of the emission currents and non-uniform turn-on voltages. Small changes in the tip radius result in huge changes in the current density because of the exponential dependence of the emitted current on the bias voltage, as described by the Fowler-Nordheim theory. If the emitters are ballasted, the spatial non-uniformity can then be substantially decreased. Furthermore, ballasting individual emitters prevents destructive emission from the sharper tips allowing higher overall current emission because of the inclusion of duller tips. Ballasting also results in more reliable operation. The use of large resistors in series with the field emitters is an unattractive ballasting approach because of the resulting low emission currents and power dissipation in the resistors. A better approach for ballasting field emitters is the use of un-gated field effect transistors that effectively provide high dynamic resistance with large saturation currents. In the past our research group demonstrated the use of a MOSFET to ballast the emission of electrons from silicon tips [1]. We plan to implement vertical un-gated transistors in series to the field emitters to obtain spatial uniformity in the current emission and I-V characteristics of the array [2]. The ballast structure is an n-doped, single-crystal silicon column, patterned using Deep Reactive Etching, and thinned using wet oxidation. Figure 2 shows a cross section of the un-gated transistors consisting of a 1-million elements in 1 cm². The field emitters are formed on top of the columns. Current efforts focus on device testing.

**Figure 1:** A) An isolated 4 µm-tall CNF on top of a 100 µm-tall silicon column; B) Zoom of the CNF tip – tip diameter equal to 36 nm; C) Field of silicon tips on top of 100 µm-tall silicon columns; D) Zoom of a silicon tip – tip diameter equal to 35 nm.

**Figure 2:** A 1000×1000 array of 100-µm-tall, 1-µm-wide silicon columns, spaced 10 µm. The columns are un-gated transistors that control the current that the tips field-emit.

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A Versatile MEMS Quadrupole Platform for Portable Mass Spectrometry Using the First and Second Stability Regions

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Sponsorship: DARPA

The Micro Gas Analyzer Program aims to develop portable, low-power, fast and low-false-alarm-rate gas analyzer technology for a wide range of applications. One of the subsystems of the gas analyzer is a mass filter. An array of micro-fabricated quadrupole mass filters is being developed for this purpose. The quadrupoles will sort out the ions based on their specific charges. Both high sensitivity and high resolution are needed over a wide range of ion masses, from 15 to 650 amu. In order to achieve this performance, multiple micro-fabricated quadrupoles, each operating at a specific stability region and mass range, are operated in parallel.

The proof-of-concept device is a single, linear quadrupole that has a micro-fabricated mounting head with meso-scaled DRIE-patterned springs. The mounting head allows micron-precision hand assembly of the quadrupole rods [1] – critical for good resolution and ion transmission. The micro-fabricated mounting head can implement quadrupoles with a wide range of aspect ratios for a given electrode diameter. The springs can be individually actuated using spring tip handlers. The current version of the spring-head is able to interact with rods with diameters from 1588 µm down to 250 µm. The quadrupoles that have been implemented thus far span the aspect ratio range from 30 to 60. The choice of electrode diameter takes into account the dimensional uncertainties and alignment capabilities with respect to the expected resolution and transmission goals. Figure 1 shows an assembled MEMS quadrupole with 250-micrometer diameter rods. Figure 2 shows the experimental data of one of these quadrupoles using FC-43 as a calibration compound, where a mass resolution of 2 amu and a full mass range of 650 amu are demonstrated, while using a 1.44 MHz RF power supply to drive the quadrupole with a constant-width circuit made by the Extrel company (Pittsburgh, PA). To obtain better resolution, the MEMS quadrupoles have been driven with up to 4 MHz RF sources, resulting in 0.7 amu peak width. Also, the devices have been driven in the second stability regions to obtain 0.4 amu of peak width and smoother peaks. Current research efforts concentrate on developing RF power supplies of higher frequency and further exploration of the second stability region to obtain better performance.

Figure 1: A micro-fabricated quadrupole with electrode diameter equal to 250 micrometers, near a dime for size comparison. The micro-fabricated part of the device is the square base, which contains a system of meso-scaled DRIE-patterned springs.

Figure 2: Experimental characterization of a MEMS quadrupole, using the compound FC-43 to get peaks in the 1 – 650 amu mass range. The peak width is estimated at 2 amu, using a 1.44-MHz-RF-power supply. Peak widths as small as 0.4 amu have been obtained.

REFERENCES
First Principles Optimization of Mass-producible Microscaled Linear Quadrupoles for Operation in Higher Stability Regions

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Sponsorship: DARPA

In recent years, there has been a desire to scale down linear quadrupoles. The key advantages of this miniaturization are the portability it enables and the reduction of pump-power needed due to the relaxation on operational pressure. Various attempts at making microscaled linear quadrupoles met with varying degrees of success [1-2]. Producing these devices involved some combination of precision machining or microfabrication and downstream assembly. For miniature quadrupole mass filters to be mass-produced cheaply and efficiently, manual assembly should be removed from the process.

A purely microfabricated quadrupole mass filter comprising a planar design and a rectangular electrode geometry is proposed. Quadrupole resolution is inversely-proportional to the square of the electrode length, thus favoring a planar design since electrodes can be made quite long. Rectangular rods are considered since that is the most amenable geometric shape for planar microfabrication. This deviation from the conventional round rod geometry calls for optimization and analysis. Electrode designs were parameterized, and the potential fields were solved using Maxwell 3D (Figure 1). The fields were decomposed using a multipole expansion to examine the higher-order coefficients (Figure 2). This process was used to minimize the significant high-order terms, thus optimizing the design and determining the ultimate limitations of the device.

Higher-order field contributions arising from geometric non-idealities lead to non-linear resonances. These resonances manifest as peak splitting that is typically observed in quadrupole mass spectra. Reported work involving linear quadrupoles operated in the second stability region show improved peak shape without these splits [3]. It is believed that operating the device in the second stability region will provide a means to overcome the non-linear resonances introduced by the square electrode geometry. This study was conducted to justify a fully microfabricated, mass-producible, MEMS linear quadrupole mass filter. Successful implementation of such devices will lead into arrayed configurations for parallel analysis and aligned quadrupoles operated in tandem for enhanced resolution.

**REFERENCES**


A Single-gated Open Architecture Carbon Nanotube Array for Efficient Field Ionization

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Sponsorship: DARPA

Mass spectrometers require a suitable ionizer to be able to discern the chemical composition of the sample that they are analyzing. Traditional ionizers for gases use either chemical ionization (CI) or electron impact ionization (EI). In the latter case, electrons from thermionic sources produce ions by colliding with neutral molecules. More efficient carbon nanotube-based field emitted electron impact ionizers have been developed [1]. However, one of the drawbacks of electron impact ionization is that the sample is transformed into fragmentation products. Several samples could have similar fragmentation spectra but be quite different compounds, with radically different properties (for example, one substance can be a poisonous agent while another is a harmless material). Therefore, an approach to reduce the fragmentation products would improve the informational power of the mass spectrometer.

Field ionization soft-ionizes molecules, thus reducing the fragmentation products. In the field ionization scheme, ions are created by directly tunneling electrons from the outer shell of neutral molecules by virtue of a very high electric field [2]. The electric field is produced by high aspect ratio field enhancers and the application of a large (up to 1 kV) bias voltage. Carbon nanotubes are ideal field enhancers because of their high aspect ratio and their reduced tip radius. A good field ionizer should work in the field-limited regime instead of the molecular flux-limited regime, where all the molecules that approach the high field region are thus ionized. In the case of the electron impact ionizers, a closed architecture is implemented because it is intended to protect the field enhancers from back streaming ions [3]. Therefore, an open architecture, where the field enhancers surround a through-hole, is a more suitable approach to produce field ionization. We plan to implement a single-gated field ionizer array with an open architecture. Figure 1 shows a schematic of the open architecture concept. Figure 2 shows a cross section of the device. Current research effort focuses on device characterization.

Figure 1: Schematic of a Field Ionizer array. The gas inlet provides neutral species to the field enhancers. If the molecules of the gas come close enough to the CNT tips, an electron from the outer shell of the molecule will tunnel to the CNT, thus ionizing the molecule.

Figure 2: A single-gated CNT field ionizer array grown at MIT. Field view of an array cross-section (A), and detail of two adjacent field ionizers (B). The ionizer well has a film of silicon dioxide 5 µm thick below the gate that acts as electrical insulator between the gate and the CNTs. The CNT catalyst was Ni 7.5 nm thick.

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Electrospray is the technique to soft-ionize liquids by applying a high electric potential to a liquid meniscus. The liquid meniscus is deformed into a cone [1], and charged species are emitted from its apex. The emission can be solvated ions, charged droplets, or a mix of the two. This low-divergence charged species source can be used in diverse applications such as mass spectrometry, propulsion, printing, and etching. Our research group has successfully developed several multiplexed MEMS electrospray sources, mainly intended for space propulsion applications. These devices include internal pressure-fed spouts that emit charged droplets [2] and externally surface tension fed spouts that emit solvated ions [3]. In all cases, the emitter field enhancers and the hydraulic impedance are provided using silicon-based structures. Furthermore, the devices use a 3D packaging technology that allows decoupling the process flows of the subsystems without loss in emitter density [4]. Consequently, it is possible to use radically different fabrication techniques and materials to implement MEMS electrospray arrays.

This project intends to investigate the application of Plasma Enhanced Chemical Vapor Deposition Carbon Nanotubes (PECVD CNTs) in multiplexed electrospray sources. Two research directions are currently pursued: the use of CNTs as hydraulic impedance to ballast the emitter array (both in internal and external architectures) and the use of CNTs as emitter field enhancers. On the one hand, PECVD CNT forests can be custom tailored to match a desired morphology. On the other hand, PECVD CNTs have remarkable field enhancing properties. Figure 1 shows a silicon-based externally fed electrospray linear emitter array that uses PECVD CNTs as hydraulic impedance, while Figure 2 shows the PECVD CNT forest grown on top of the silicon structures, using our group’s reactor. Current research is focused on exploring the wettability of CNT forests using different liquids, catalysts, and growth conditions. These results will be used to choose the proper nanostructure to be used in an externally fed MEMS electrospray head that will eventually include CNT-based field enhancers.

**REFERENCES**


Near-room-temperature Processed Metal Oxide Field Effect Transistors for Large-area Electronics

Sponsorship: Hewlett-Packard

Recently, sputtered metal-oxide-based field effect transistors (FETs) have been demonstrated with higher charge carrier mobilities, higher current densities, and faster response performance than amorphous silicon FETs, which are the dominant technology used in display backplanes [1-2]. Furthermore, the optically transparent semiconducting oxide films can be deposited in a near-room-temperature process, making the materials compatible with future generations of large-area electronics technologies that require use of flexible substrates [3]. It is possible to process FETs by shadow-mask patterning, but this method limits the range of feature sizes, accuracy of pattern alignment, and scalability of the process to large substrates. Consequently, our project aims to develop a low-temperature, lithographic process for metal oxide-based FETs, similar to one developed for organic FETs [4], that can be integrated into large-area electronic circuits.

Using an organic polymer, parylene, as the gate dielectric and indium-tin-oxide (ITO) for source/drain contacts, top-gate, lithographically processed FETs have been fabricated on glass substrates using ZnO:In$_2$O$_3$ channel layers. Figure 1 shows a micrograph of a completed FET, with current-voltage characteristics shown in Figure 2.

A reproducible FET process requires consistent control of material properties of the metal oxide semiconductor film. We examine the effect of varying deposition conditions (e.g., target composition, O$_2$ partial pressure, film thickness) and post-deposition treatment on DC- and RF-sputtered amorphous oxide thin films in the In$_2$O$_3$-ZnO system. The electrical properties of thin films are determined through resistivity and Hall measurements. These measurements are used as a guide to determine processing conditions for the fabrication of oxide-based field effect transistors and circuits.

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Field Emission from Double-gated, Isolated, Vertically Aligned Carbon Nanofiber Arrays
Sponsorship: DARPA

A collimated electron beam is often desired to achieve high performance for practical applications such as field emission display and ebeam lithography. We designed and fabricated a double-gated, isolated, vertically aligned carbon nanofiber field emission array (VACNF FEA) to produce a collimated electron beam. The first gate is used to extract electrons out of the tip and the second gate (focus gate) is biased at a lower voltage than the first gate to focus the emitted electrons.

In this work, we designed a device that maximizes the electric field generated at the tip and minimizes the shield effect from the neighbor while it is capable of handling a large breakdown voltage during the field emission operation. To accomplish this, an isolated VACNF with 4-µm-tall per emission site is needed with each site 10µm apart. The e-beam lithography and lift-off were used to define a 250-nm-diameter and 4-nm-thick Ni catalyst on an n-type Si substrate to guarantee nucleation of Ni dots and subsequent growth of CNFs. The 4-µm-tall VACNF was grown using plasma-enhanced chemical vapor deposition at 725°C. Once the CNF was synthesized, the extraction gate and the out-of-plane focus gate were fabricated with a novel photo-resist planarization technique. This technique offers a very fast, fairly uniform, and well-controlled planarization method of making the self-aligned gate, which can replace the CMP technique that has been reported and used by L. Dvorson et al., M.A. Guillorn et al., and L.-Y. Chen et al. [1-3]. This abstract is perhaps the first report of double-gated, self-aligned, field emitter arrays with isolated VACNF.

With this fabrication process, two types of devices were fabricated: (1) with tip in-plane with the extraction gate and (2) CNF with tip 900nm below the extraction gate. They were characterized as three-terminal devices (focus and extraction gate at same bias) and as four-terminal devices (focus and extraction gates at different biases). Figure 1 shows a scanning electron microscope (SEM) picture of a complete device. Using this device, a four-terminal current-voltage (I-V) measurement was performed. As the focus voltage increases, the anode current increases, which is shown in Figure 2.

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Electron Impact Ionization and Field Ionization of Gas through Double-
gated, Isolated, Vertically Aligned Carbon Nanofiber Arrays


Sponsorship: DARPA

The goal of this project is to fabricate double-gated carbon
nanofiber field emission and field ionization arrays, which can
be utilized as an ionizer in a micro gas sensor. This device can
help reduce the power consumption and the size of the conven-
tional gas sensor. To achieve this goal, the double-gated isolated
VACNF device is designed so that the electric field is maximized
at the tip and the shielding effect from the neighbor is minimized
while it is capable of handling a large breakdown voltage dur-
ing the field emission and field ionization operations. Using a
photoresist-based fabrication process, two types of devices were
fabricated: (1) CNF with tip in-plane with the gate and (2) CNF
with tip 0.9µm below the gate. Both devices have the following
physical characteristics: (a) The tip height is about 4µm, (b) the
gate diameter is 1.7µm, and (c) the focus diameter is 4.2µm. Fig-
ure 1 shows a scanning electron microscope (SEM) picture of a
complete double-gated isolated vertically aligned carbon nanofi-
ber (VACNF) array with tip 0.9µm below the gate.

Using the device shown in Figure 1, electron impact ionization
and field ionization methods of ionizing gas molecules were per-
formed. The electron impact ionization uses a strong electric
field to emit electrons followed by collisions between the energetic
electrons and neutral gas molecules, resulting in ionization. A lin-
ear relationship was obtained between the chamber pressure and
the ratio of the ion current and the electron current, as shown in
Figure 2. The field ionization is a gentler process in comparison
to electron impact ionization. Instead of electrons tunneling from
the tip to the vacuum under a high field (as in field emission), in
field ionization, electrons tunnel from the gas molecules into the
tip, thereby ionizing the gas molecules. It results in molecular
ionization and a simpler mass spectrum due to less fragmentation
of molecules.

Figure 1: An SEM picture of a complete isolated VACNF array
with tip 0.9µm below the gate.

Figure 2: The linear relationship between the pressure and
the ratio of the ion current and the emission current in electron
impact ionization.
Integrated Organic Circuits and Technology for Large Area Optoelectronic Applications

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Sponsorship: SRC/FCRP C2S2

Organic semiconductors can be deposited at near-room temperatures, enabling the creation of electronic and optoelectronic devices on virtually any substrate. This unique technology makes possible the fabrication of large-area, mechanically flexible optoelectronics, such as conformable displays or image sensors. To realize these systems, an integrated approach to fabrication of organic optoelectronics is necessary.

A near-room temperature (<95°C), scalable process has been developed, using conventional photolithography and inkjet printing [1]. This process produces integrated organic field effect transistors (OFETs) and organic photoconductors (OPDs) on a single substrate. A cross section of the finished substrate is shown in Figure 1.

Typical device characteristics for an integrated OFET are shown in Figure 2. As a proof of concept, a 4x4 active-matrix imager was created using the process and was demonstrated to correctly image patterns [2].

References