Compact, 3D-Printed Electron Impact Ion Source with Microfabricated, Nanosharp Si Field Emitter Array Cathode

Chenye Yang and Luis Fernando Velásquez-García
Microsystems Technology Laboratories, Massachusetts Institute of Technology, Cambridge, MA 02139 USA

Email: jasony84@mit.edu, Velasquez@alum.mit.edu

Abstract. We report the design, fabrication, and characterization of a novel miniature electron impact gas ionizer manufactured via silicon micromachining and high-resolution 3D printing. The ionizer uses an array of 2,500 gated silicon nano-sharp field emitters (20 μm emitter pitch) as cathode and a set of additively manufactured, finely featured polymer and metallic parts as three-dimensional ion-generating structure. Finite element simulation of a gated field emitter tip predicts a start-up bias voltage equal to 64 V – close to the 62 V turn-on bias voltage estimated via experiments. The Si field emitter array emits 124.5 μA of electron current with ~60% gate transmission while operating at 200 V. The ionization efficiency of the gas ionizer is linear with pressure, reaching values as high as ~0.4% at 5×10^-4 Torr.

1. Introduction

Mass spectrometry is a mainstream chemical analytical technique used to quantitatively determine the composition of a sample via ionization and mass-to-charge ratio species sorting. State-of-the-art mass spectrometer (MS) systems are bulky, heavy, and power-hungry, which restricts their applicability. Consequently, significant research has been conducted with the aim to develop MS systems that are small, light, and low-powered to be able to satisfy in-situ applications such as geological survey, law enforcement, environmental monitoring, and industrial process monitoring [1]-[4].

For gas and volatile samples, ion generation is typically achieved via electron impact ionization, where energetic electrons collide with neutral molecules to create charged species [5]. State-of-the-art electron impact ionizers (EIIs) utilize a thermionic cathode. However, thermionic electron sources are not ideal for miniaturized MS systems because their high-temperature (> 2,000 K) electron-emitting surface [6] is at odds with the aim of compact MS systems to relax the vacuum requirements [7].

An attractive alternative to thermionic cathodes for compact mass spectrometry is a field emission cathode in which electrons are quantum tunnelled from the surface of metals and semiconductors to vacuum due to the presence of a high local electric field (≥3×10^7 V/cm) that lowers and narrows the potential barrier that holds the electrons within the material. Field emission cathodes consumes less power and respond faster than thermionic cathodes. Field emission cathodes use high-aspect-ratio tips to generate high local electric fields with moderate bias voltages.

This paper reports the design, fabrication, and characterization of a novel, miniature EII for gases composed of a Si micromachined cold cathode and an additively manufactured three-dimensional ion-generating structure. Unlike metal-based field emission tips, Si tips can withstand oxygen at moderate pressure without degradation [9]. Unlike reports of EIIs with a 2D flat metal grid that defines the
ionization region [10], our device uses a 3D high-transparency metal cage to define a constant-potential region, which increases the effective electron impact ionization cross-section, resulting in higher ionization efficiency at the same pressure.

2. Device design and simulation

The proposed EII, shown in figure 1, is composed of a silicon micromachined cold cathode chip and a 3D-printed ion-generating structure made of polymer and metallic parts. The silicon chips were manufactured using CMOS batch microfabrication, not only to uniformly create very small features (e.g., nanosharp tips), but also to increase the fabrication yield of the devices. The ion-generating structure was 3D-printed to allow for fast prototyping, low-cost manufacturing, and compatibility with three-dimensional designs that are more efficient at generating ions than two-dimensional designs.

The cathode is a 10 mm by 10 mm silicon chip with 3 electrically independent arrays of 2,500 nanosharp, gated tips (20 $\mu$m emitter pitch). The Si chip is held by two custom PCBs that allow easy selection and interfacing with any of the tip arrays. The chip-PCBs assembly is seated on top of a 3D-printed resin base, and 4 Nylon fasteners are used to secure the ion-generating structure to the resin base.

The 3D-printed ion-generating structure is composed of four 3D-printed components, i.e., ion cage, electron collector, ion repeller, and cap. The ion cage is a barrel-like electrode that sets a region with

![Figure 1](image1.png)

Figure 1. (a) Optical image and (b) schematic of compact EII with Si field emission cathode and 3D-printed ion-generating structure. The Si chip (lower right corner of (a)) is held by two PCBs.

![Figure 2](image2.png)

Figure 2. Finite element simulation of a gated Si tip with +75 V DC applied to the gate and the Si substrate grounded. The tip surface electric field is $\sim$3.5x10^7 V/cm; therefore, at least $\sim$64 V are needed to trigger electron tunnelling to vacuum.

![Figure 3](image3.png)

Figure 3. Selected views of process flow to create Si field emission array: (a) isotropic and anisotropic etch to partially create Si tips; (b) tip sharpening via oxidation; (c) oxide deposition; (d) oxide planarization; (e) aperture etching on silicon nitride film; (f) oxide release and Pt deposition.
uniform electric potential, resulting in a uniform ionization cross-section across the region, which increases the ionization efficiency of EII if the potential is optimized; the lateral side of the ion cage is a high-transparency, monolithic mesh with 340 \( \mu \)m diameter wires. The electron collector electrode gathers the electrons emitted by the cathode and released during ionization of the sample molecules. The ion repeller electrode pushes the ions out of the ion cage toward the ion collector. The cap assembles the electrodes into a three-dimensional structure while providing insulation to each of the electrodes.

Finite element simulations of a gated field emitter tip (figure 2) were conducted with the commercial software COMSOL. The simulations predict a \(~64\) V start-up bias voltage (\(~3 \times 10^7\) V/cm tip surface electric field; gate electrode is biased positive with respect to the silicon substrate that is grounded).

3. Device fabrication

This section describes the fabrication of the field emission cathode and the ion-generating structure.

3.1. Fabrication of silicon cathode

The fabrication of the field emission cathode, inspired by previous work [11],[12], uses as starting substrate a 6-inch, n-type, 500 \( \mu \)m-thick, double-side polished silicon wafer (0.02 \( \Omega \)-cm resistivity); selected steps of the process flow are shown in figure 3. First, a film stack consisting of a 100 nm-thick thermal silicon dioxide film, a 100 nm-thick silicon-rich silicon nitride film, and a 500-nm-thick plasma-enhanced chemical vapour deposited (PECVD) silicon dioxide film are grown and deposited on the wafer. Then, alignment marks are etched on the top side of the wafer. After that, the film stack is dry etched to form 2.2 \( \mu \)m diameter discs –each disc serves as hard mask for patterning an emitter. Next, a sulphur hexafluoride (SF\(_6\))-based isotropic dry etch is used to etch the exposed silicon substrate, undercutting the discs and forming partially sharpened tips with a neck diameter (diameter of the emitter at the point of contact to the hard mask) equal to 200 to 300 nm. The exposed silicon is further etched using a chlorine-based anisotropic dry etch step that increases the height of the emitters without changing the neck diameter (figure 3a). Afterwards, thermal oxidation is performed to fully sharpen the tips to \(~6\) nm in diameter. After the oxidation, diluted hydrofluoric acid and hot phosphoric acid are used to strip oxide films and nitride films, releasing the emitters (figure 3b).

Creation of the proximal gate starts by depositing a 5-\( \mu \)m-thick PECVD silicon dioxide film that fully covers the emitter tips, followed by annealing of the film in nitrogen at 950°C for 30 minutes (figure 3c). The wafer is then planarized via chemical mechanical polishing (CMP, figure 3d). Next, the PECVD dioxide is etched using an anisotropic etch recipe, all the way to the silicon substrate, followed by a 0.5-\( \mu \)m-deep anisotropic etch of the exposed silicon –creating the mould for the gate’s stand-offs. After that, 0.85-\( \mu \)m-thick silicon-rich silicon nitride is deposited; the nitride film is dry etched to pattern gate apertures, each of them concentric to an emitter tip. Afterwards, buffered oxide etch (BOE) is used to completely remove the PECVD silicon dioxide layer (figure 3e). The fabrication of the proximal gate is completed by depositing a thin layer of evaporated platinum to make the gate electrically conductive and protect the emitter tips (figure 3f).

3.2. Fabrication of ion-generating structure, base

The dielectric part of the ion-generating structure and the ionizer base were printed in Solus Proto resin via high-resolution digital light projection-stereolithography (DLP-SLA), while the metal parts of the ion-generating structure are printed in SS 316L via high-resolution binder inkjet printing.

4. Experimental characterization

This section reports the characterization of the Si chip as electron source while operating in a high vacuum (2\( \times 10^{-7}\) Torr), and the characterization of the EII using air in the 1.6\( \times 10^{-7}\) to 5\( \times 10^{-4}\) Torr range. The Si field emission cathode emits 124.5 \( \mu \)A of electron current with \(~60\)% gate transmission while operating at 200 V. The ionization efficiency of the EII is linear with pressure, reaching values as high as 0.4% at 5\( \times 10^{-4}\) Torr.
4.1. Field emission tests

4.1.1. Setup. The characterization of the silicon cathodes in triode configuration was conducted in a custom vacuum chamber with a turbo and a diaphragm pump that can reach pressures down to $1 \times 10^{-8}$ Torr. In the tests the substrate is grounded, the gate is biased at a positive voltage, and a collector electrode (a 46 mm-diameter flat plate suspended ~8 mm above the gate) is biased at +1100 V.

4.1.2. Cathode I-V characteristics and FN plot. Figure 4 shows a typical I-V characteristic of the field emitter arrays. The turn-on voltage is ~62 V, in good agreement with the 64 V predicted by the finite element simulations. When the gate-to-substrate bias voltage is set at 200 V, the gate transmits 73.7 $\mu$A (~60% of the emitter current). Field emission is described by the Fowler-Nordheim (FN) equation \[ I_E \propto \beta^2 \cdot V_G^2 \cdot \exp \left( \frac{-6.49 \times 10^7 \phi^{1.5}}{\beta V_G} \right) \] (1)

where $I_E$ is the emitted current of an emitter biased at a voltage $V_G$, $\beta$ is the field factor of the tip in cm$^{-1}$ (approximately equal to $3.82 \times 10^6 r_{tip}^{-0.89}$, with $r_{tip}$ the tip radius in nanometres [11]), and $\phi$ is the work function of the emitting surface in eV. Figure 5 shows the FN plot of the data shown in figure 4, i.e., $\ln(I/E/V_G^2)$ versus $1/V_G$ for different voltages. From equation (1), field emitted current describes a straight line with slope $-6.49 \times 10^7 \phi^{1.5}/\beta$ in the FN plot. Therefore, from the slope of the linear fit a field factor equal to $1.49 \times 10^6$ cm$^{-1}$ assuming 6.35 eV of workfunction for Pt, or ~6 nm of tip diameter, which agrees with SEM metrology of the tips (inset figure 5).

4.2. Electron impact ionization tests

4.2.1. Setup. EIIs were characterized by leaking air into the previously described vacuum chamber to set the vacuum level between $1.6 \times 10^{-7}$ and $5 \times 10^{-4}$ Torr. In these experiments the gate is grounded, the silicon substrate is biased at a voltage between 0 V and -170 V to trigger field emission of electrons, the ion cage is biased at +60 V to maximize the ionization cross-section, the repeller is biased at +80 V to push ions out of the ion cage, and the ion collector (an external electrode used to collect the ion current) is biased at -20 V and placed ~1 cm away from the ion source.

4.2.2. EII I-V characteristics. Figure 6 shows the I-V characteristics of the device at $5 \times 10^{-4}$ Torr, producing 0.13 $\mu$A of ion current while the field emission cathode is emitting 32.5 $\mu$A electron current though its gate. Therefore, the ionization efficiency of the device, i.e., the ion current-to-electron current ratio, is ~0.4% at such pressure. Figure 7 shows the ionization efficiency versus pressure data of an EII;
a power-law least-squares fitting of the data suggests that there is a linear dependence between the two variables—in agreement with the electron impact ionization model. From the least-squares fitting, an average total ionization cross-section equal to $1.5 \times 10^{-16}$ cm$^{-2}$ is obtained—close to the total maximum ionization cross section for diatomic nitrogen and oxygen (the main components of air) reported in [13].

5. Conclusions
We reported the design, fabrication, and characterization of a novel miniature electron impact gas ionizer manufactured via silicon micromachining and high-resolution 3D printing. The ionizer has an array of gated silicon nano-sharp field emitters as cathode and a set of additively manufactured, finely featured polymer and metallic parts as three-dimensional ion-generating structure. The Si field emission cathode emits 122.8 $\mu$A of electron current with 60% gate transmission while operating at 200 V. The ionization efficiency of the EII is linear with pressure, reaching values as high as 0.4% at $5 \times 10^{-4}$ Torr.

Acknowledgement
This work was sponsored in part by the IARPA’s MAEGLIN program (award FA8650-17-C-9103, program manager Dr. Kristy DeWitt). Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the US Government and therefore, no official endorsement of the US Government should be inferred.

References
[1] Diaz J A et al. 2015 J. Am. Soc. Mass Spectrom. 26 (2) 292-304
[2] Sanders N L et al. 2010 Anal. Chem. 82 (12) 5313-6
[3] Li L et al. 2014 Anal. Chem. 86 (6) 2909-16
[4] Hamilton S E et al. 2013 Org. Process Res. Dev. 18 (1) 103-8
[5] Gross J H 2006 Mass spectrometry: a textbook (New York, NY: Springer)
[6] Herring C and Nichols M H 1949 Rev. Mod. Phys. 21 (2) 185
[7] Ferran R J and Boumsellek S 1996 J. Vac. Sci. Technol. A Vac. Surf. Films 14 (3) 1258–65
[8] Gomer R 1993 Field Emission and Field Ionization (New York, NY: AIP)
[9] Fomani A A, Akinwande A I and Velásquez-García L F 2013 J. Phys. Conf. Series 476 012014
[10] Velásquez-García L F, Gassend B L P and Akinwande A I 2010 J. Microelectromech. Syst. 19 (3) 484-93
[11] Basu A Swanwick M E, Fomani A A and Velásquez-García L F 2015 J. Phys. D: Appl. Phys. 48 (22) 225501
[12] Cheng S, Hill F A, Heubel E V and Velásquez- García L F 2015 J. Microelectromech. Syst. 24 (2) 373–83
[13] Straub H C et al. 1995 Phys. Rev. A 52 (2) 1115