Low-cost, additively manufactured electron impact gas ionizer with carbon nanotube field emission cathode for compact mass spectrometry

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Abstract

We report the design, fabrication, and experimental characterization of the first additively manufactured electron impact gas ionizer for compact mass spectrometry in the literature. The device occupies a total volume equal to 2.3 cm$^3$ and is composed of a carbon nanotube (CNT) field emission electron source and a multi-material, 3D-printed multi-electrode ion-generating structure. The ionizer’s electron source is a silicon chip coated with a forest of plasma-enhanced chemical vapour deposited CNTs as emitting substrate and a 100 µm thick stainless-steel stencil with thousands of 100 µm diameter apertures at 150 µm aperture pitch as extraction gate. The device’s ion-generating structure is a set of 3D-printed, finely featured dielectric and metallic parts that kindle interaction between electrons and neutrals and shepherd ions outside the structure; its dielectric components were printed in polymer via high-resolution digital light projection stereolithography (25 µm pixels), while its metallic pieces were binder inkjet-printed in SS 316L with features as small as 340 µm (thickness of the wires of the ion cage). The CNT field emission electron sources were experimentally characterized in high vacuum ($2.0 \times 10^{-7}$ Torr), emitting up to 1.4 mA @ 700 V with 31.5% gate transmission. The ionizers were characterized in air at pressures as high as 5 mTorr, generating up 38 µA ion current with 8.5% ionization efficiency. The ion current is linear with pressure, in agreement with the electron impact ionization model.

Keywords: 3D-printed microsystems, CNTs, compact mass spectrometry, electron impact ionization, field emission

(Some figures may appear in colour only in the online journal)
source converts neutral molecules into charged fragments, i.e. ions; the mass filter sorts these ions according to their mass-to-charge ratios using electric and/or magnetic fields; the detector measures the ions transmitted by the mass filter; the vacuum pump keeps one or more subsystems at a pressure level at which the subsystem(s) can satisfactorily operate. There are numerous reports of miniaturized MS components manufactured via standard microfabrication including mass filters [10–17], detectors [18], and vacuum pumps [19–23].

Reported work on MEMS ionizers for gases focuses on electron impact ionization, where energetic electrons convert neutral molecules to ions via fragmentation [24, 25]. State-of-the-art electron impact gas ionizers for MS systems use a thermionic cathode as electron source; however, these devices have disadvantages for a portable instrument, e.g. the need to heat up a surface to high temperature (>1725 °C) to achieve electron emission [26] is at odds with the overall aim of compact MS systems to work at low-vacuum (>10^{-4} Torr) [27].

Cold cathodes emit electrons into vacuum via quantum tunnelling due to high surface electric fields that lower and narrow the barrier that traps electrons within the material; typically, high-aspect-ratio, nano-sharp tips are used to produce a high enough local electric field (~3 × 10^9 V m^{-1}) to trigger field emission with moderate bias voltages [28, 29]. Compared to thermionic cathodes, field emission electron sources have faster response and less power consumption [30, 31]. The reliability of cold cathodes is typically affected by back-ion bombardment and chemical degradation [32, 33]; in particular, metal-based [34] and silicon-based cold cathodes [35] degrade when exposed to traces (>10^{-6} Torr) of oxygen [36, 37].

Carbon nanotube (CNT)-based cold cathodes are attractive for implementing electron impact ionizers (EIIs) for compact MS because of CNTs’ remarkable physical and chemical properties including very high aspect-ratio, nano-sized tip radius, and resistance to back-ion bombardment and chemical degradation [38, 39]. Consequently, there are numerous reports of CNT EIIs [40–44]; however, these devices are microfabricated using cleanroom technology and/or use ion-generating structures machined with standard technologies, affecting their cost and size.

Additive manufacturing (AM) are bottom-up fabrication techniques that create, layer by layer, designs described by a computer-aided design (CAD) model [45]. AM has unique advantages over traditional manufacturing methods including complex geometry compatibility, print customization, waste reduction, prototyping time reduction, and cost reduction [46]. In recent years, AM technology has been used to demonstrate miniaturized systems that outperform counterparts made in a cleanroom [47–50], including novel designs that are challenging to construct with standard microfabrication methods [51, 52], e.g. because they involve complex 3D shapes [53].

This paper reports the design, fabrication, and characterization of the first EII for compact mass spectrometry in the literature. The device is based on a CNT field emission cathode and a high-resolution, multi-material, 3D-printed ion-generating structure; unlike miniature EIIs with a 2D flat metal grid that defines the ionization region, e.g. [43, 44], this 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. Section 2 describes the design of the CNT EII. Section 3 explains the fabrication of the CNT EII. Section 4 reports the vacuum outgassing of the printed material. Section 5 describes the experimental characterization and data analysis of the CNT field emission electron source and CNT EII. Section 6 summarizes the work.

2. Device design

The CNT EII reported in this paper is composed of two subsystems, i.e. a CNT-based field emission electron source and a 3D-printed ion-generating structure (figure 1). The CNT field emission electron source (figure 2) is composed of an emitting substrate (i.e. silicon chips coated with a field forest of plasma-enhanced chemical vapour deposited (PECVD) CNTs attached to a 10 mm by 10 mm silicon substrate), a gate electrode (i.e. a 100 μm-thick stainless-steel flat plate with...
100 \, \mu m \text{ diameter apertures and } 150 \, \mu m \text{ aperture pitch), and a set of stand-offs made in 99.5\% \text{ alumina that provide electrical insulation between the emitting substrate and the gate while setting a narrow, uniform gap between them. The Si substrate is held between two custom printed circuit boards (PCBs). The overall design of the ionizer is inspired on that of commercial electron impact counterparts that employ specialized, 3D electrodes to accomplish different tasks, e.g. electron collection, ion generation. Additionally, the design is intended to be compatible with operation at mTorr-level pressure; the mean free path at such pressure is around a few centimetres, which is the upper limit of the dimensions of the ionizer to avoid ions colliding with neutrals after they are formed. The choice of the electron source is consequent with the aim to be compatible with operating at such pressure; in contrast, thermionic electron sources quickly degrade at such vacuum level, and field emission cathodes with metal or Si tips do not have the same resilience of CNTs while operating at low vacuum [36, 37].}

The ion-generating structure was 3D-printed to allow for fast prototyping, low-cost manufacturing, and compatibility with 3D designs that are more efficient at generating ions than 2D designs. The 3D-printed ion-generating structure is composed of four components (three electrodes and one dielectric part), i.e. ion cage, electron collector, ion repeller, and cap. The ion cage (figure 3(a)) is a barrel-like electrode that surrounds a region with uniform electric potential—the volume in which the ions are created, resulting in a uniform effective ionization cross-section across the region, which increases the ionization efficiency of EII if the potential is optimized. The lateral surface of the ion cage is a high-transparency square mesh made of 340 \, \mu m \text{ by } 340 \, \mu m \text{ wires; the wires are tilted } 45^\circ \text{ from the horizontal to facilitate its manufacturing (in general, overhangs with } 45^\circ \text{ to } 90^\circ \text{ inclination with respect to the build plate are easier to print consistently). The electron collector (figure 3(b)) gathers the electrons emitted by the cathode, as well as the electrons released during ionization. The ion repeller (figure 3(c)) pushes the ions out of the ion cage towards the ion collector (e.g. the inlet of the mass filter, or an external electrode). The cap (figure 3(d)) interfaces with the electrodes to create a 3D structure while providing electrical insulation to each of the conductive components.

A key consideration for the specification of the geometries and dimensions of the ionizer is the capabilities of the AM methods and printers employed, as well as the physical properties of the printed materials; in particular:

- The smallest features of the design should be significantly larger than the voxels of the printer, and the overall
dimensions of the parts should be considerably larger than the size of the smallest features. The printers employed in this study use voxels with characteristic length of a few tens of micrometres, and are capable of resolving with good accuracy features on the order of a few hundred micrometres (see section 3.2).

- The printed materials should not emit constitutive feedstock in vacuum, and the outgassing level should be compatible with vacuum operation; this is the case for both the dielectric and metal printed materials (see section 4).
- The selected AM methods should be capable of producing the geometries of the different components without the need of dummy features or post-processing. For example, the printing methods used to create the dielectric [54] and metal parts [55] do not require support/dummy structures that need to be dissolved/clipped after printing (see section 3.2).

3. Device fabrication

In this section, the fabrication and assembly of the additively manufactured CNT EII is described.

3.1. Fabrication of PECVD CNT chips

The fabrication of the electron-emitting substrates starts with a single-sided polished, 6-inch, n-type Si wafer that is cleaned using a mix of sulfuric acid and hydrogen peroxide, to then be rinsed in deionized water and dried with nitrogen. Next, the wafers are coated with a 5 nm-thick evaporated Co film that serves as catalyst of CNT growth. After that, the wafer is put in a PECVD reactor where annealing of the film in a reducing environment at Torr level pressure takes place at 650 °C, boiling up the film into nanospheres. The wafer then sees an acetylene-based plasma at 815 °C at Torr level pressure that grows ~15 µm-tall CNTs using the Co nanospheres as template. In PECVD, the nanospheres move away from the substrate while precipitating a carbon nanotube that is firmly attached to the substrate; the catalyst nanosphere eventually gets coated with a layer of carbon, stopping the growth process. The wafer is then broken into pieces ~2 mm in side.

3.2. Fabrication of ionizer base and components to implement ion-generating structure

The dielectric components of the ion-generating structure, as well as the base plate of the EII, were printed in SolusProto resin (Junction 3D, Santa Clarita CA, USA) using CAD files in STL format and a Solus digital light projection/stereolithography (DLP/SLA) printer (Junction 3D, Santa Clarita CA, USA) that has 25 µm × 25 µm pixels; the layer thickness was set at 30 µm. After printing, the parts were sequentially rinsed in 90% isopropyl alcohol to remove uncured resin, followed by immersion in water with detergent, and rinsed in clean water. Afterwards, the prints were dried with an air gun. Post-curing of the parts was done with a UV chamber for 10 min.

In a recent study, our group reported the minimum feature size, repeatability, and fidelity of the printed part to the CAD model for DLP/SLA-printed SolusProto resin [56]. Metrology of resolution matrices (flat plates with arrays of straight circular pillars that systematically cover a range of diameters and heights) revealed minimum feature size as small as 75 μm, in-plane printed offset (on the plane defined by the build plate) of 14 μm, and out-of-plane offset (perpendicular to plane of the build plate) of 16 μm. In addition, the least-squares fittings of the data suggest linearity between the printed dimensions and the corresponding CAD dimensions, with a 1.6% difference in the printed in-plane dimensions and a 0.6% difference in the out-of-plane dimensions; these differences are repeatable and therefore, the CAD files can be compensated to correct to first order the mismatch. The minimum feature size and fidelity of SolusProto are significantly better than those from any other commercial DLP/SLA resin we are aware of (e.g. [57]). The surface roughness of the SolusProto printed parts was characterized using a confocal microscope (Mitutoyo Quick Vision ACTIVE 202, Mitutoyo America Corporation, Marlborough, MA, USA), resulting in an average arithmetic mean height \( S_a \) equal to 277 nm ± 31 nm. The dielectric constant of printed SolusProto was characterized using flat-parallel capacitors with electrodes made of copper tape. The capacitors were assembled and kept at 20% RH before characterization at 10 kHz, 1 V using a tweezers-style LCR meter LCR Pro1 (LCR Research, Toronto, Ontario, Canada) with 0.1% accuracy. The dielectric constant of printed SolusProto is estimated at 3.99 ± 0.06, which is similar to the dielectric constant of stereolithography-printed Somos® 9120 resin (DSM Functional Materials, Somos® Material Group, Elgin IL, USA) [58].

The conductive parts of the ion-generating structure were binder inkjet-printed in SS 316L with a DM P2500 printer (Digital Metal, Hollsopple PA, USA) at room temperature. The tool has ~30 µm × 30 µm in-plane pixels and prints in ~35 µm-thick layers. The binder is digitally applied to agglomerate the feedstock powder on specific regions of each layer following a CAD STL file. After carefully removing any loose powder, the parts are annealed at ~1360 °C in a Torr-level nitrogen atmosphere to eliminate trapped air and densify the print. The printed part shrinks during annealing due to the high porosity of the non-compacted feedstock powder; however, the amount of shrinkage is repeatable, allowing compensation of the CAD files. Finally, the parts are carefully polished. In a recent study, our group reported the minimum feature size, repeatability, and fidelity of the printed part to the CAD model for binder inkjet-printed SS 316L [59]. Metrology of the matrices revealed minimum feature size as small as 285 µm, in-plane printed offset of 10 µm, and out-of-plane offset of 25 µm. In addition, the least-squares fittings of the data suggest linearity between the printed dimensions and the corresponding CAD dimensions, with a 3.2% difference in the printed in-plane dimensions and a 1.7% difference in the out-of-plane dimensions; these differences are repeatable and therefore, the CAD files can be compensated to correct to first order the mismatch. Compared to direct metal laser sintering (the most commonly used AM method for metal) of SS 316L,
binder inkjet printing of SS 316L has associated smaller in-plane offset and out-of-plane offset, and the prints have visibly less porosity [59]. The surface roughness of the SS 316L printed parts was characterized using a confocal microscope (Mitutoyo Quick Vision ACTIVE 202, Mitutoyo America Corporation, Marlborough, MA, USA), resulting in an average arithmetic mean height $S_A$ equal to 2.364 $\mu$m $\pm$ 0.319 $\mu$m.

### 3.3. CNT EII assembly

Several PECVD CNT chips are attached to a 10 mm by 10 mm silicon substrate using SEM tape, and the silicon substrate is secured to a PCB with conductive pads covered with SEM tape, making electrical connection between the PCB and the silicon substrate. A plurality of PECVD chips were used instead of a single chip covering the same total area to ensure that more CNTs would emit electrons (this approach places more CNTs at the edge of a CNT field forest, which is the region of the forest at which the CNTs have the weakest electric field shadowing). Next, the ceramic stand-offs are attached to the silicon substrate and to the gate using Kapton tape. After that, a second PCB is placed on top of the gate electrode, making electrical connection between the PCB and the gate. The Si-PCBs assembly is then seated on top of the 3D-printed resin base, and wires are soldered to the PCBs to be able to provide bias voltages to the gate and to the emitting substrate. The ion-generating structure is assembled using the cap to integrate the ion cage, electron collector, and ion repeller; the parts were designed to work like Lego (e.g. with small-interference interlocking features). Finally, four Nylon fasteners are used to secure the ion-generating structure to the resin base to complete the ionizer. The ionizer occupies a total volume equal to 2.3 $cm^3$ (the equivalent of a 1.3 cm-wide cube).

### 4. Outgassing characterization

This section reports the vacuum outgassing characterization of the 3D printed components to address the fact that the reported ionizer is intended to operate in vacuum. Both vacuum outgassing rates and mass spectrometry of the outgassing are provided.

The vacuum outgassing of binder inkjet-printed SS 316L and DLP/SLA-printed SolusProto resin was characterized using a custom testing rig composed of a 200 mm wide ultra-high vacuum (UHV)-compatible SS cube chamber fitted with a 200 amu reduced gas analyser (Hiden Analytical, Peterborough NH, USA) that can measure partial pressures as small as $7.5 \times 10^{-15}$ Torr. The system is pumped by a 68 l s$^{-1}$ dry rough pump/turbo combo capable of reaching $7.5 \times 10^{-11}$ Torr ultimate pressure (if baked). The samples tested are printed flat plates with nominal surface area equal to 96 $cm^2$. Measurement of the outgassing rates was conducted every ten minutes for over 10 h. A summary of the experimental results at 1 h 10 h are provided in table 1. As expected, the majority of the outgassing in both samples is water (the samples were not baked in vacuum).

| Sample       | H$_2$O | C$_x$H$_y$ | H$_2$O | C$_x$H$_y$ |
|--------------|--------|------------|--------|------------|
| SS 316L     | 40.5   | 27.8       | 5.4    | 2.6        |
| SolusProto  | 4125   | 2700       | 1800   | 1050       |

The 10 h outgassing rate of binder inkjet-printed SS 316L after subtracting the contribution of water vapor is equal to $2.8 \times 10^{-9}$ Torr l$(s cm^{-2})$, which is adequate for UHV applications [60]. After 10 h of continuous pumping, the partial pressure of hydrocarbons mixed in the vacuum is about two orders of magnitude smaller than the contribution from water vapor; this is supported by the lack of peaks above 69 amu in the 10 h mass spectrum (figure 4).

The 10 h outgassing rate of DLP/SLA-printed SolusProto after subtracting the contribution of water vapor is equal to $7.5 \times 10^{-7}$ Torr l$(s cm^{-2})$, which is in the range reported for common vacuum-compatible elastomers, e.g. fluoroelastomer, Buna-N ($10^{-5}$–$10^{-7}$ Torr l$(s cm^{-2})$) [61]. After 10 h of continuous pumping, the partial pressure of hydrocarbons mixed in the vacuum is more than three orders of magnitude smaller than the contribution from water vapor; this is supported by the lack of peaks above 69 amu in the 10 h mass spectrum (figure 5), evidencing that the printed part is not ejecting constitutive material to vacuum.
to ~245 V (emission current of ~2 μA with 8.5% ionization efficiency).

The start-up voltage of this device is equal to 700 V, and the maximum current transmitted by the gate is 446 μA electron current transmitted by the gate (31.5% of the emitted current). Characterization of the ionizer at pressures between 2.7 × 10⁻⁷ Torr and 5 × 10⁻³ Torr resulted in ion currents as large as 38 μA with 8.5% ionization efficiency. No evidence of device degradation after prolonged characterization of the ionizer was noticed, e.g. due to thermal expansion, dimensional mismatch.

5. Experimental characterization and discussion

In this section, the PECVD CNT electron source and the EII are characterized in a vacuum chamber. Characterization of the field emission electron source at 2 × 10⁻⁷ Torr yielded up to 446 μA electron current transmitted by the gate (31.5% of the emitted current). Characterization of the ionizer at pressures between 2.7 × 10⁻⁷ Torr and 5 × 10⁻³ Torr resulted in ion currents as large as 38 μA with 8.5% ionization efficiency. No evidence of device degradation after prolonged characterization of the ionizer was noticed, e.g. due to thermal expansion, dimensional mismatch.

5.1. Characterization field emission electron source

5.1.1. Apparatus. The PECVD CNT ionizers were tested in a triode configuration inside a grounded vacuum chamber at ~2.0 × 10⁻³ Torr while being pumped down by a turbo and a diaphragm pump. The silicon substrate was grounded, the gate voltage was varied between 0 V and +700 V, and an external collector electrode (a 46 mm-diameter flat plate suspended ~6 mm above the gate electrode) was biased at +1100 V. When the substrate-to-gate bias voltage is large enough and the gate is at a higher potential than the Si substrate, CNTs attached to the silicon substrate quantum tunnel electrons, a portion of which are transmitted through the gate (i.e. gathered by the collector electrode), while the rest of the electrons is intercepted by the gate. For practical purposes, there is no physical connection between the collector electrode and the silicon substrate of the gate electrode.

5.1.2. I–V characteristics—electrons. Figure 6 shows typical current–voltage (I–V) characteristics of a CNT field emission electron source. The start-up voltage of this device is equal to ~245 V (emission current of ~2 × 10⁻¹⁰ A), and the maximum current transmitted by the gate is 446 μA when the bias voltage between the emitting substrate and the gate is equal to 700 V. The gate current is dominated by leakage through the stand-offs for bias voltages between 200 V and ~245 V; after the device activates, the emitter current, intercepted current, and transmitted current are parallel in the semi-log plot, evidencing linearity between the currents, which is further supported by figure 7. This suggests that the currents are field emitted and have a common source. From the slope of the

least-squares fitting in figure 7, the transmission rate of gate is estimated at 31.5%.

5.1.3. FN analysis. Field emission is described by Fowler–Nordheim (FN) equation [62]

\[ I_E(V_G) \propto \beta^2 \cdot V_G^2 \cdot \exp \left( \frac{-6.49 \times 10^7 \cdot \phi^{1.5}}{\beta \cdot V_G} \right) \] (1)

where \( I_E \) is the electron current emitted by a tip biased at a voltage \( V_G \) with respect to the gate, \( \beta \), in cm⁻¹, is the field factor of the tip (to first order equal to the inverse of the tip radius of the emitter for a CNT forest facing a flat gate [44]), and \( \phi \) is the work function of the emitting surface in eV. Figure 8 shows the FN plot of the emitted and transmitted data shown in figure 6, that is, a plot of \( \ln(I/G(V_G)) \) versus \( V_G^{-1} \). Equation (1) predicts that field emitted current describes a straight line with slope equal to \(-6.49 \times 10^7 \cdot \phi^{1.5}/\beta \) in the FN plot. The slope of the two least-squares fittings in figure 8 is very close, further corroborating the idea that the currents have the same source. From the slopes of the linear fittings, an average field factor equal to 1.32 × 10⁵ cm⁻¹ is estimated assuming 4.81 eV as the work function for carbon, corresponding to ~150 nm tip diameter; this value compares well with SEM metrology of the CNT tips (inset figure 8).

5.2. Characterization electron impact ionizer

5.2.1. Apparatus. The compact CNT EII was characterized by leaking air into the previously described vacuum chamber; during each test the chamber pressure was held constant, but different tests were run at different pressure levels that fell in the 2.7 × 10⁻⁷ Torr to 5 × 10⁻¹ Torr. Running the ionization experiments requires five power supplies to apply an equal number of independent biasing voltages as follows: the gate is biased at 0 V to ground it, the silicon substrate is biased at voltage between 0 V and ~700 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 an external a flat plate ~1 cm away from the ion source is biased at ~20 V to collect the ions.

5.2.2. I–V characteristics—ions. Figure 9 shows typical characteristics of ion current versus silicon substrate-to-gate bias voltage for chamber pressures between 2.7 × 10⁻⁷ Torr.
and and 5.0 × 10⁻³ Torr. The device was successfully operated at 5 × 10⁻³ Torr with no degradation while generating ion currents as high as 38 µA with 8.5% ionization efficiency, i.e. ion current-to-transmitted electron current ratio. For a given electron current, the exponent of the power law, least-squares fitting of the data shown in figure 10 (0.985) suggests that the ionization efficiency has a linear dependence on the pressure, as expected from the electron impact ionization model [63]. The coefficient of the least-squares fitting (16.272) predicts an average total ionization cross-section equal to 6.6 × 10⁻¹⁶ cm⁻², within a factor of two of the maximum total ionization cross sections for Ar, N₂, and O₂ (the main constituents of air) reported by Straub et al [64, 65]. The coefficient of the power-law least-squares fit is at least a threefold larger than previously reported CNT EII coefficients [43, 44]; therefore our devices produce significantly more ions for the same electron current, gas, and gas pressure.

The reported results compare well with the literature. For example, Bower et al reported a MEMS CNT EII with ~1% ionization efficiency for Xe and ~0.1% ionization efficiency for Ar while operating at 5 mTorr [44]; their device has similar ionization length compared to our device, but it has the issue of a non-uniform ionization region previously described. In addition, the slopes of the FN plot in our device are 33% smaller than the FN slope in the work of Manohara et al [42]; given that both devices use CNTs as electron field emitters, our device has a higher field factor and therefore, it emits more current for the same bias voltage.

In our opinion, the main reason for the superior performance of our ionizer compared to the reported work on similar devices that have a CNT electron source is the implementation of an ionization region with constant ionization cross-section. In the reported work [42–44], the ionization region does not have a constant bias voltage because is defined with a perforated flat plate, which results in a non-uniform electron impact cross-section across the space where ions are created. The 3D, glove-like geometry of the ionizer cage in our design is what makes possible defining an ionization region with uniform cross-section. 3D printing makes possible to implement such part at a low cost (it is possible to bond a large stack of microfabricated wafers to make an ionization cage of comparable dimensions, but it would be time consuming and very expensive). In addition, compared to commercial and reported [66, 67] electron impact gas ionizers with thermionic cathodes, the use of carbon nanotubes as electron source allows operating the ionizer at orders of magnitude lower vacuum, which significantly increases the ionization efficiency.

6. Conclusion

We reported the design, fabrication, and experimental characterization of the first additively manufactured electron impact gas ionizer for compact mass spectrometry in the literature. The device is composed of a PECVD CNT field emission
electron source and a 3D, multi-material, additively manufactured ion-generating structure, resulting in a device design that is simple, low-cost, and easy to put together. Vacuum outgassing characterization of the 3D-printed metal shows UHV compatibility, while characterization of the 3D-printed polymer shows HV compatibility and outgassing rates similar to those of common vacuum-compatible elastomers. The PECVD CNT field emission electron sources were tested at 2.0 × 10⁻⁷ Torr, producing up to 1.4 mA of electron current with 31.5% transmission through the gate (i.e., 446 µA) while being biased at 700 V. The gas ionizer was characterized in air at pressures between 2.7 × 10⁻⁷ Torr and 5.0 × 10⁻³ Torr; the device generated ion currents as high as 38 A with 8.5% ionization efficiency. The ionization efficiency of the device is linear with pressure, in agreement with the electron impact ionization model.

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References

[1] Shortt B J, Darrach M R, Holland P M and Chutjian A 2005 Miniaturized system of a gas chromatograph coupled with a Paul ion trap mass spectrometer J. Mass Spectrom. 40 36–42
[2] Prieto M C, Kivotou V V and Cotter R J 2002 Miniaturized linear time-of-flight mass spectrometer with pulsed extraction J. Mass Spectrom. 37 1158–62
[3] Huang Y, Li J, Tang B, Zhu L, Hou K and Li H 2015 Development of a portable single photon ionization-photoelectron ionization time-of-flight mass spectrometer Int. J. Anal. Chem. 2015 581696
[4] Diaz J A, Giese C F and Gentry W R 2001 Sub-miniature ExB sector-field mass spectrometer J. Am. Soc. Mass Spectrom. 12 619–32
[5] Snyder D T, Pulliam C J, Ouyang Z and Cooks R G 2015 Miniature and fieldable mass spectrometers: recent advances Anal. Chem. 88 2–29
[6] Bada J L and McDonald G D 1996 Peer reviewed: detecting amino acids on Mars Anal. Chem. 68 668A–73A
[7] Hamilton S E, Mattrey R, Bu X, Murray D, McCullough B and Welch C J 2013 Use of a miniature mass spectrometer to support pharmaceutical process chemistry Org. Process Res. Dev. 18 103–8
[8] Diaz J A et al 2015 Unmanned aerial mass spectrometer systems for in situ volcanic plume analysis J. Am. Soc. Mass Spectrom. 26 292–304
[9] Yang M, Kim T Y, Hwang H C, Yi S K and Kim D H 2008 Development of a palm portable mass spectrometer J. Am. Soc. Mass Spectrom. 19 1442–5
[10] Wapelhorst E, Hauschild J P and Müller J 2007 Complex MEMS: a fully integrated TOF micro mass spectrometer Sensors Actuators A 138 22–7
[11] Pau S, Pai C S, Low Y L, Moxom J, Reilly P T A, Whitten W B and Ramsey J M 2006 Microfabricated quadrupole ion trap for mass spectrometer applications Phys. Rev. Lett. 96 120801
[12] Kanu A B, Dwivedi P, Tun M, Matz L and Hill H H 2008 Ion mobility–mass spectrometry J. Mass Spectrom. 43 1–22
[13] Taylor S, Tunstall J J, Symr R R A, Tate T and Ahmad M M 1998 Initial results for a quadrupole mass spectrometer with a silicon micromachined mass filter Electron. Lett. 34 546–7
[14] Cheung K, Velásquez-García L F and Akinwande A I 2010 Chip-scale quadrupole mass Filters for portable mass spectrometry J. Microelectromech. Syst. 19 469–83
[15] Symr R R A, Tate T J, Ahmad M M and Taylor S 1998 Design of a microengineered electrostatic quadrupole lens IEEE Trans. Electron. Dev. 45 2304–11
[16] Gecar M, Symr R R A, Wright S and Holmes A S 2005 Monolithic MEMS quadrupole mass spectrometers by deep silicon etching J. Microelectromech. Syst. 14 1156–66
[17] Velásquez-García L F, Cheung K and Akinwande A I 2008 An application of 3-D MEMS packaging: out-of-plane quadrupole mass filters J. Microelectromech. Syst. 17 1430–8
[18] Riehl P S, Scott K L, Muller R S, Howe R T and Yasaitis J A 2003 Electrostatic charge and field sensors based on micromechanical resonators J. Microelectromech. Syst. 12 577–89
[19] Kim H, Astle A A, Najafi K, Bernal L P and Washabaugh P D 2007 A fully integrated high-efficiency peristaltic 18-stage gas micropump with active microvalves Proc. IEEE 20th Int. Conf. Micro Electro Mechanical Systems pp 131–4
[20] Taylor A P and Velásquez-García L F 2017 Miniaturized diaphragm vacuum pump by multi-material additive manufacturing J. Microelectromech. Syst. 26 1316–26
[21] An S, Gupta N K and Gianchandani Y B 2014 A Si-micromachined 162-stage two-part Knudsen pump for on-chip vacuum J. Microelectromech. Syst. 23 406–16
[22] Basu A and Velásquez-García L F 2016 Electrostatic ion pump with nanostructured Si field emission electron source and Ti particle collectors for supporting ultra-high vacuum in miniaturized atom interferometry systems J. Micromech. Microeng. 26 124003
[23] Grzebyk T, Görécka-Drazga A, Dziuban J A, Zawada A and Konarski P 2014 Micropump for generation and control of vacuum inside miniature devices J. Microelectromech. Syst. 23 50–5
[24] Hauschild J P, Wapelhorst E and Müller J 2007 Mass spectra measured by a fully integrated MEMS mass spectrometer Int. J. Mass Spectrom. 264 53–60
[25] Tassetti C M, Mahieu R, Daniel J S, Peyssonneaux O, Progent F, Polizzi J P, Machuron-Mandard X and Duraffourg L 2013 A MEMS electron impact ion source integrated in a microtime-of-flight mass spectrometer Sensors Actuators B 189 173–78
[26] Herrington C and Nicholas M H 1949 Thermionic emission Rev. Mod. Phys. 21 185
[27] de Hoffmann E, Charrette J and Stroobant V 1997 Mass Spectrometry: Principles and Applications (Hoboken, NJ: Wiley)
