Electrospray from arrays of miniaturised all-photopolymer emitters

IEPC-2017-207

Presented at the 35th International Electric Propulsion Conference
Georgia Institute of Technology – Atlanta, Georgia – USA
October 8–12, 2017

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Arrays of 16 and 380 microemitters, consisting of capillaries with less than 50 micrometres diameter and a length of up to 80 micrometres, were patterned photolithographically in SU-8 negative tone photoresist. Electrospray current of the ionic liquid EMI-BF_4 drawn from these arrays by an external high voltage was characterised for both DC component and AC component up to a frequency of 11 kilohertz. To achieve stable emission, the diameter of the capillaries has to be reduced further, among others. It is proposed to use three-dimensional microlithography for this purpose, and first results of a feasibility study are presented.

Nomenclature

Symbols

I	emission current
σ_I	standard deviation of emission current
$\bar{I}$	mean (time-averaged) emission current
t	time
V_{ext}	external (extraction and acceleration, combined) voltage

Abbreviations and acronyms

EMI-BF4	1-ethyl-3-methylimidazolium tetrafluoroborate (an ionic liquid)
HVS	high voltage source
PEEK	polyether ether ketone (a polymer resistant to high temperatures)
SEM	scanning electron microscope/microscopy
SU-8	(an expoxy-based negative tone photoresist)

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I. Introduction

Electrospray thrusters offer a way of extending electric propulsion to the regime of low thrust and small impulse bits, at low system volume requirements and without moving parts. This makes them interesting both for deep space high precision missions[1] ("LISA-like missions"), but also for the propulsion of the evolving class of very small satellites, exemplified by CubeSats.[2] The operating principle of electrospray thrusters is that the propellant, usually an ionic liquid, is transported from the tank via a small diameter channel, the capillary, to the capillary's outward orifice. Under the influence of an electric field, applied between the ionic liquid and an extraction electrode, the liquid at the capillary's orifice forms a sharp tip, the Taylor cone. The very high local electric field strength at the Taylor cone's tip leads to the emission of small droplets of charged ionic liquid, and, under ideal conditions, eventually to the emission of pure ions. These ions can be further accelerated by another electrode and thus provide the thrust. With a suitable choice of ionic liquid, the emission of both positive and negative ions can generate thrust. The ambipolar operation of electrospray thrusters, either by alternating the polarity of the individual thrusters or by operating some individual emitters at positive and others at negative voltage simultaneously, thus has the potential of eliminating the need for an additional neutraliser.

Most conventionally made thrusters are too large for CubeSats. Electrospray thrusters offer the possibility of miniaturisation by orders of magnitude because they can be fabricated using technologies from the field of micro electro mechanical systems (MEMS), which in turn have their roots in the microelectronics technology. Most research groups that have been or are actively pursuing fabrication of electrospray thrusters in MEMS technology make use of the various microfabrication methods of silicon technology,[3] including photolithography, crystallographic etching and high aspect ratio deep etching.[4] Silicon technology has the advantage that a complete set of technologies both in front end production and in back end finishing (packaging, e. g. by bonding or glueing) are in place. The disadvantage of silicon technology, a planar technology at its core, is that the design rules, imposed mostly by the crystalline nature of silicon, limit the freedom of design especially when the design becomes more complex in the dimension vertical to the plane.

An alternative to silicon as the material of construction is the use of a photostructurable polymer like SU-8.[5] This epoxy polymer is stable against high temperatures and corrosive chemicals, making it a material of choice in the fields of microfluidics and lab-on-a-chip. It can also be used as a photoresist in a process chain involving pattern transfer, where it offers unsurpassed possibilities of creating high aspect ratio microstructures with heights of tens or even hundreds of micrometres. In this application, however, the stability of SU-8 against chemical attack limits the choice of resist removal methods and, consequently, the choice of functional materials, to e. g. metals or alloys that withstand oxygen plasma etching.[6]

Miniaturisation of emitters opens the pathway to a completely new way of designing thrusters. Instead of tailoring thrusters to the ranges of thrust and impulse bits required by the individual mission by redesigning parts of the thruster, microthrusters with unchanged design can be operated in parallel to work as one thruster with the desired parameters. The performance of the individual microemitters, such as a high specific impulse[7] expected to be above 1000 s for miniaturised electrospray emitters in silicon technology,[8] should not be influenced in this process, known as "scaling-up by numbering-up".

In the following, we present results on the electrspray emission from arrays of microemitters, made in planar technology. We also show how three-dimensional microlithography has the potential of relieving many of the restrictive design rules of today's planar technologies.

II. Experimental work and results

We have previously shown that the microfabrication of electrospray emitters in SU-8 by multilayer (two-dimensional) planar lithography can be used to generate both the capillary layers as well as an extraction electrode support layer and the intermediate spacer layer.[9,10] Electrospray from individual microemitters was characterised by optical telemicroscopy in this initial work. The test stand has been modified according to Fig. 1 to allow the measurement of the electric (ionic) current drawn from the microemitters. The experimental work concentrates on the capillaries, and consequently the extraction electrode has been placed outside the sample for the work reported here. It usually consisted of a metallic ring with an inner diameter of up to a few millimetres, placed at a distance of up to ten millimetres from the capillary orifices. The extraction electrode was connected to ground, and the extraction voltage was applied to the ionic liquid reservoir ("tank"), where the propellant was held in place by gravity. Experiments were carried out both with negative

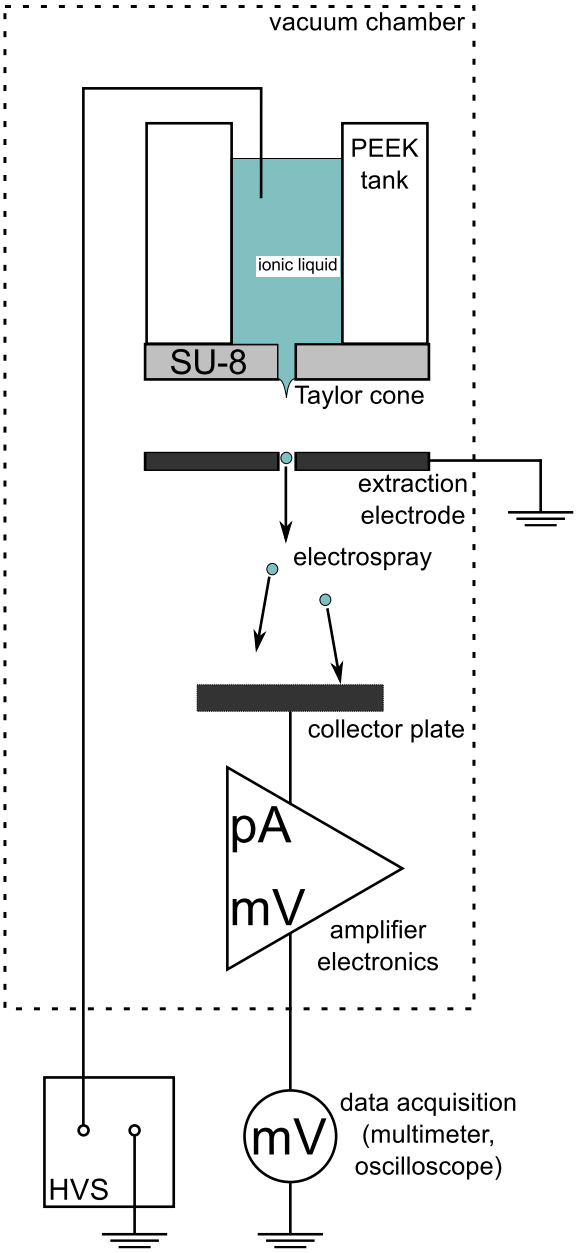

Figure 1. Schematic drawing of the measurement setup for the electrical characterisation of electrospray emitters. The high voltage source can have either polarity.

as well as with positive high voltage. Measurement cycles were kept so short that no appreciable charging of the reservoir took place, and neutralisation during the measurement did not need to be considered. There was no additional acceleration electrode, so the external voltage is the only voltage providing extraction and acceleration.

The electrospray current passing the extraction electrode was collected on a conducting plate, usually made of copper, and discharged to ground via amplifier electronics placed inside the vacuum chamber. The amplified signal's DC component was continuously acquired using a digital multimeter and stored on a computer. A digital oscilloscope allowed the acquisition of the AC component of the current signal, which was also recorded by the computer, up to a cutoff frequency limited by the amplifier electronics of approximately 11 kHz.

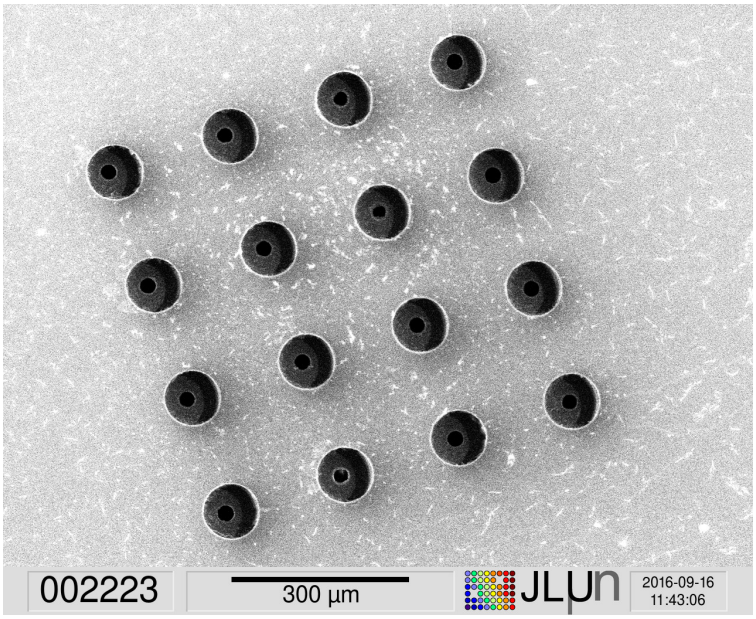

Figure 2. Scanning electron microscopy (SEM) image of an array of 16 microemitters made by two-dimensional photolithography of SU-8 resist. The diameter of the capillaries is approximately 30 µm. In this sample, a second lithography was used to create a spacer layer with circular openings of approximately 100 µm diameter. Both layers had a thickness of approximately 35 µm.

A. Arrays of emitters fabricated by 2D photolithography

The process flow for the emitters was reported earlier.[5] An SU-8 layer (SU-8 50, supplied by microchemicals.com) with a thickness of between 35 and 80 µm was spincoated onto a 2 inch silicon wafer and exposed by broadband ultraviolet (UV) lithography in a Suss MA-56 mask aligner through a photomask supplied by a commercial vendor. In the exposed regions, the SU-8 undergoes a crosslinking reaction, making it insoluble in the developer (mr-Dev 600, supplied by microchemicals.com). Optionally, before development, a second lithography aligned to the capillary layer lithography could be employed to create a spacer layer. Since the spacer layer openings are in close proximity to the capillary orifices, they need to be taken into account when the wetting of the SU-8 surface by the ionic liquid is considered, since electrospray impacting the spacer layer sidewalls could accumulate and create electric shortcuts, eventually limiting the useful life of the emitters.

After development, the supporting silicon wafer was dissolved in a warm potassium hydroxide solution bath in the course of approximately six to eight hours. The remaining SU-8 membrane was dried, cut in pieces, and the individual samples were glued to sample holdes made of a vaccum compatible plastic material.

The smaller arrays investigated has four by four microemitters arranged on a square grid with 200 µm pitch, as shown in Fig. 2.

Emission from an array as the one shown in Fig. 2, with the extraction electrode at a distance of approximately 10 mm, started at a negative external voltage of approximately 2 kV as shown in Fig. 3 (left hand panel). In the right hand panel of Fig. 3, the standard deviation of the ionic current over time has been plotted as a measure of the fluctuation of the current in the respective points of operation. With increasing external voltage, these fluctuations, believed to result from Rayleigh instabilities of the Taylor cone, decrease, until a stable emission (within the 11 kHz frequency limit of the amplifier electronics) is reached around 3 kV external voltage. While the standard deviation only gives an indication of the amplitude of the instability of the current, the oscilloscope traces shown in Fig. 4 reveal the periodic nature of the fluctuations. At the onset of emission, the instabilities manifest themselves as spikes in the emission current occurring at a frequency of approximately 10 Hz. With increasing voltage, the frequency of the instabilities increases, until at around 3 kV any oscillations remaining can no longer be resolved by the measurement electronics.

The hysteresis in the left hand panel of Fig. 3 already indicates that homogeneity of emission from the arrays may be an issue. This is further illustrated by the left hand panel of Fig. 5 which shows the DC component of the emission current as a function of external voltage for the first ramping-up of the voltage on this sample and for subsequent ramping-ups a few minutes later. The onset of the emission is rather

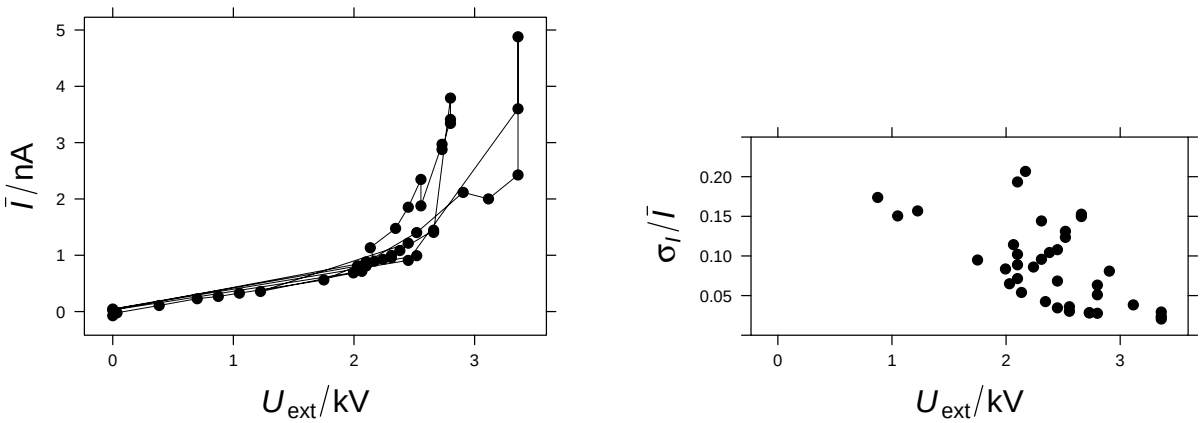

Figure 3. Left hand panel: time-averaged emission current as a function of external voltage for the measurement series from which the data in Fig. 4 were taken, showing the onset of emission at a voltage of approximately 2 kV. As the voltage was ramped up and down repeatedly, both the hysteresis in the respective traces as well as the fact that the traces deviate from each other for higher currents indicate that not all emitters started up or shut down at the same voltages. Right hand panel: relative standard deviation of the current, decreasing as the stable regime of emission is reached above an external voltage of approximately 3 kV.

sharp the first time. In subsequent runs, the emission starts at a lower extraction voltage, and the onset is smoother. This indicates that not all capillaries may have been equally filled with propellant from the beginning. The remaining inhomogeneity of emission certainly has to be a subject of further investigation.

Note that in the measurement shown in the left hand panel of Fig. 5, the emission current is that high that the measurement electronics went into saturation. It is worth mentioning that in the case of this sample, the capillary diameters were on the order of only 20 µm and thus the lowest for all measurements presented here. The systematic dependence of emission current on capillary diameter remains a subject of investigation. Data gathered earlier had already indicated that to achieve stable emission, the capillary diameter should not exceed 40 µm given our usual SU-8 layer parameters.[11] Data on the magnitude of the emission current as a function of capillary diameters are too scarce for a conclusion at this point in time.

Inhomogeneities should to a certain degree smooth out as the number of microemitters in the arrays is increased, albeit at the price of different electric fields and different emission onsets at the individual microemitter sites. In the right hand panel of Fig. 5, the emission currents captured from two arrays of 16 and 380 microemitters, respectively, have been normalised to the number of microemitters and plotted for comparison. When comparing the absolute value of the emission current with other measurements shown here, it should be kept in mind that in this case the capillary diameters were approximately 50 µm and thus at the upper limit of diameters for stable operation.

B. Fabrication of emitters by 3D microlithography

An intermediate conclusion that can be drawn from the data presented above is that the capillaries should have a diameter on the order of ten micrometres at a length of more than 30 µm. The aspect ratio of appromimately 3 demanded by this requirement can in principle be met with 2D photolithography of SU-8. However, in combination with the stacked multi-lithography process flow needed to integrate a spacer layer and extraction electrodes, this technique with its design rules meets its limits. The most restrictive design rule is that every layer of remaining resist has to reside on a continuous column of resist all the way to the substrate, in other words, there can be no undercut profiles. For optimised ion optics, more freedom of design for the layers above the capillary orifices is certainly desirable.

The novel technique of three-dimensional microlithography available in the Nanoscribe brand of equipment offers a way to relieve many of the design rules restricting 2D lithography. In 3D microlithography, the substrate is dip-coated with a liquid or jelly resist, either SU-8 or another resist specialty with comparable properties. A femtosecond laser whose photon energy is too small to cause the photochemical reaction responsible for the exposure of the resist is then directed into the resist through a microscope objective.

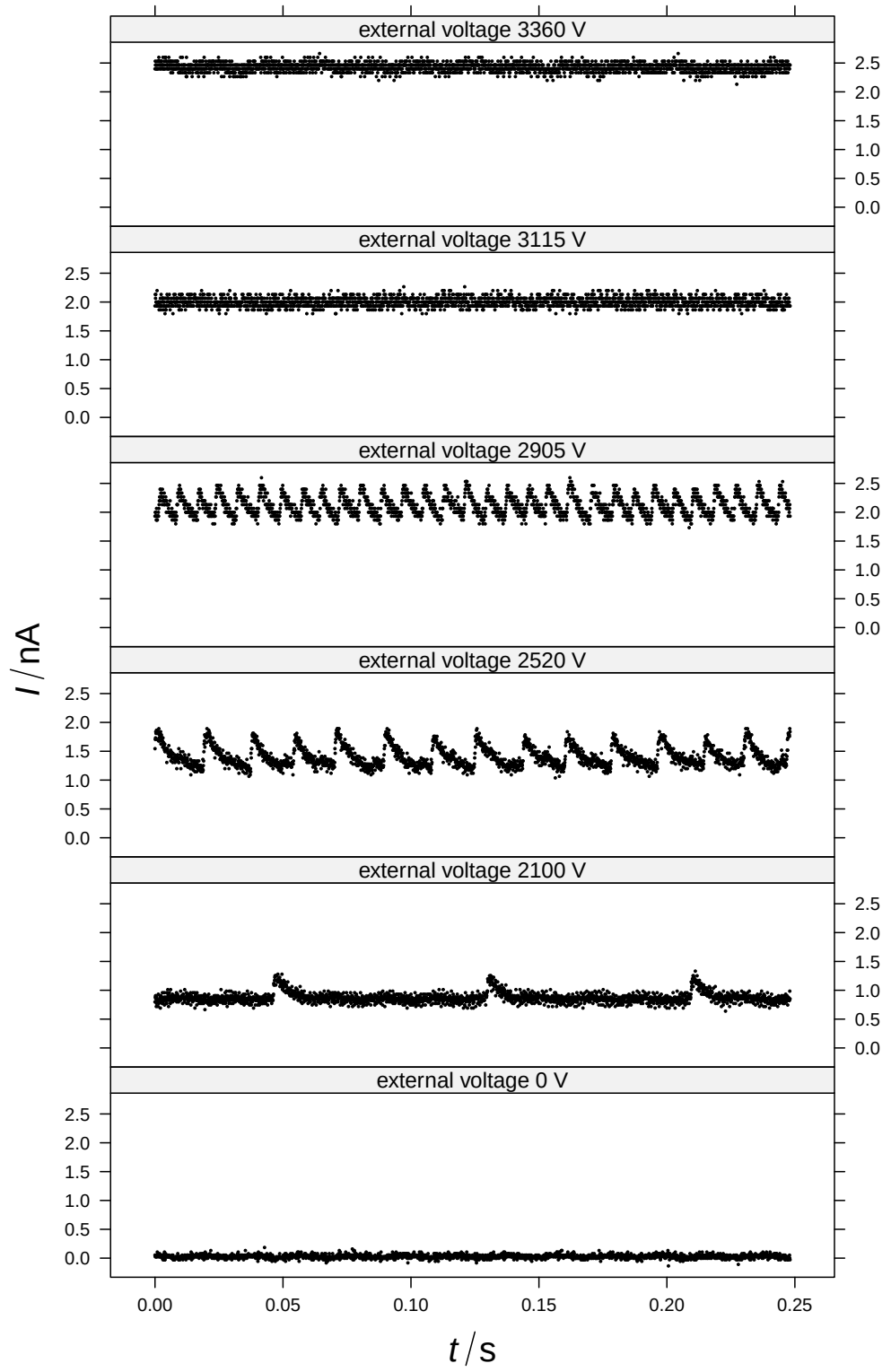

Figure 4. Series of time-resolved emission current measurements from a 4×4 array of planar microemitters for different values of the external (extraction and acceleration) voltage (distance approx. 10 mm). Instabilities appearing at the onset of emission increase in frequency with increasing voltage, until a stable emission is reached around an external voltage of approximately 3 kV.

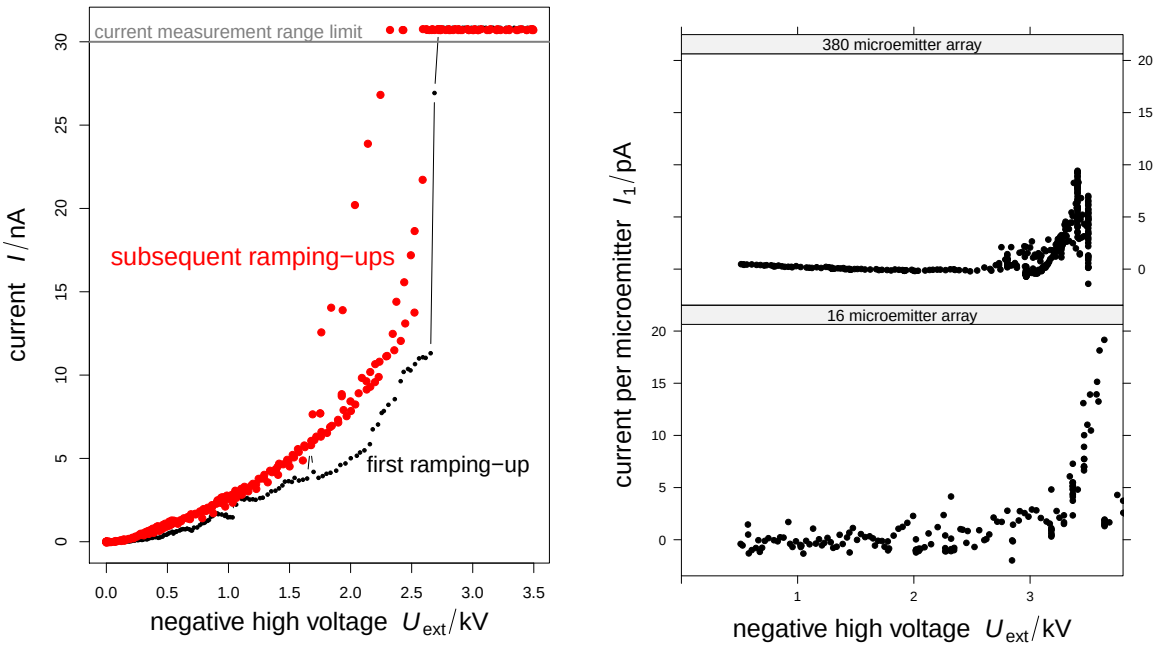

Figure 5. Left hand panel: ionic current from an array of 16 microemitters as a function of external (combined extraction and acceleration) voltage for the first (small black dots) and subsequent (large red dots) ramping-ups of the external voltage. The onset of emission occurs at a lower voltage and becomes smoother in later ramping-ups, indicating a non-homogeneous filling and emission behaviour of the capillaries. Right hand panel: comparison of the emission currents from two arrays with different numbers of microemitters, normalised to the number of microemitters. Both measurements were taken using the same extraction electrode geometry, and both samples had capillary diameters of 50 µm in SU-8 layers of (40±5) µm thickness. The current per microemitter is roughly the same under these circumstances.

Around the focus of the objective inside the resist, the light intensity is that high that two-photon absorption processes occur and that the photochemical reaction takes place. The volume element in which the resist is thus exposed is on the order of three wavelengths of light in the direction perpendicular to the plane and less than a wavelength of light in the directions parallel to the plane. By scanning the laser beam through the resist pool, three-dimensional structures can be exposed with a great freedom of design.

Examples of demonstrator structures relevant to the fabrication of electrospray microemitters are shown in Fig. 6. In the left hand panel, a tapered emitter ("volcano emitter") has been fabricated, aligned to a hole in an SU-8 substrate membrane. Such tapers are desirable since they mitigate the problem of wetting of the SU-8 by the ionic liquid.[9] In the same lithography step, a spacer layer with an undercut profile supporting a resist plane structure at a vertical distance of approximately 35 µm from the substrate has been patterned. To show the three-dimensional features, half of the circular structure has been omitted. The right hand panel shows that with this technique, capillary orifices with diameters smaller than 2 µm can be fabricated.

For the fabrication of the structures shown in Fig. 6, the laser beam remained fixed relative to the microscope optics, and the sample (substrate with dip-coat resist pool) was moved by means of piezo actuators. In this "piezoscan" mode, writing times of the Nanoscribe instrument are an issue. To save writing time, only the surfaces of the structures were written directly. After development, the hardened surfaces contained resist that was still liquid. This resist was solidified in a subsequent exposure flood exposure step. To avoid distortion of the structures, the thickness of the surface elements written had to be optimised, trading off against writing time.

With the latest generation of 3D microlithography instrumentation, however, writing time has become less of an issue. In addition to the piezoscan mode, the Nanoscribe instruments offer the additional capablity of scanning the laser beam by means of mirrors along the beam path ("galvoscan"). For structures like the one in the left panel of Fig. 6, galvoscan mode reduced the writing time from hours to minutes.

Volcano emitter structures written with Nanoscribe in galvoscan mode are shown in Fig. 7. Process optimisation to give the desired shape of the tapers is still required, and although the writing time is short,

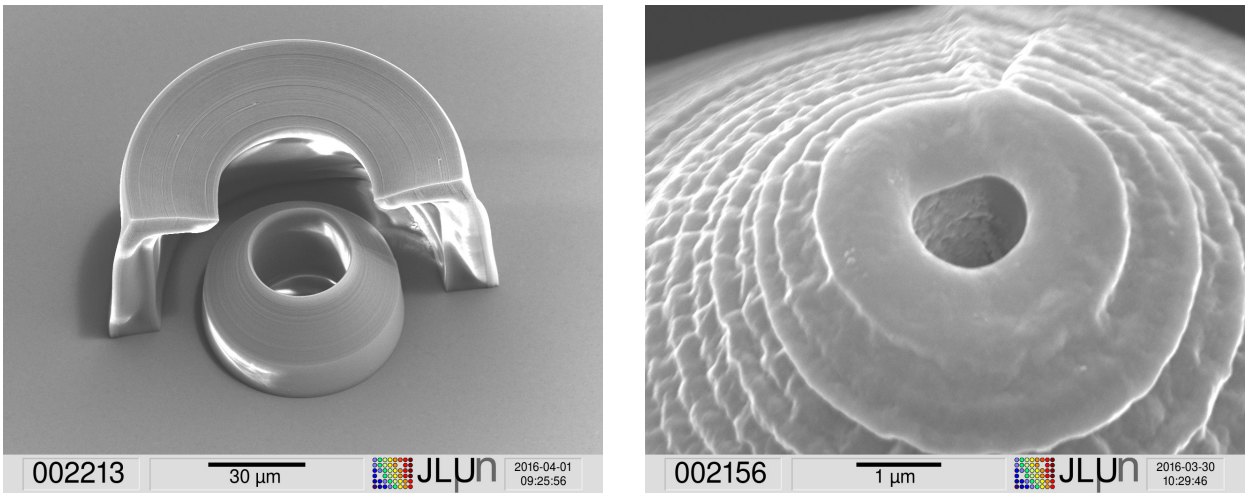

Figure 6. SEM images of demonstrator structures fabricated with Nanoscribe 3D microlithography. Left hand image: volcano emitter, aligned to a hole in the substrate pre-patterned by 2D photolithography of SU-8 resist, along with a demonstrator structure for a combined spacer and extraction electrode support layer. The latter has been written over one half-circle only to show the three-dimensional structure. Right hand image: orifice of a volcano emitter with a diameter of less than 2 micrometres, showing the small residual surface roughness of the structures caused by the stepwise scanning in the direction perpendicular to the substrate.

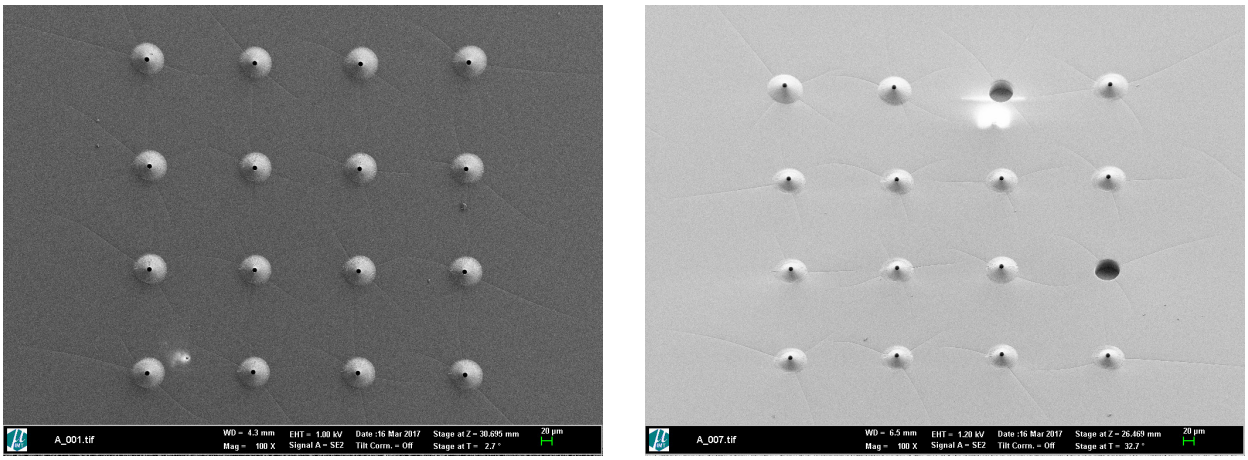

Figure 7. SEM images of arrays of four by four volcano emitters, fabricated by Nanoscribe 3D microlithography on substrates pre-patterned by 2D photolithography of SU-8 resist. In the right hand image, two volcanoes were omitted in order to show the size of the holes in the substrate.

alignment of the structures written to the pre-fabricated holes in the SU-8 membrane substrate currently limits the throughput. However, as the 3D microlithography instrumentation currently aiming at the research market may evolve into devices suitable for fabrication, there is no technical obstacle to an automation and hence speeding-up of this step.

It should be noted that the emitter diameters in all Nanoscribe-made array samples are smaller or even much smaller than what can be routinely achieved by 2D lithography with broadband exposure. This offers one pathway to tailoring the fluidic resistance of the propellant feed capillaries.[12] Another way of increasing the fluidic resistance is to use high aspect ratio macroporous silicon substrates, available commercially from smartmembranes.de. Figure 8 shows how both planar lithography as well as 3D microlithography can be aligned to the macropores in the silicon substrates. The process flow does not have to be altered substantially for lithography on these substrates, however, the spincoating or dipcoating steps have to be adapted slightly.

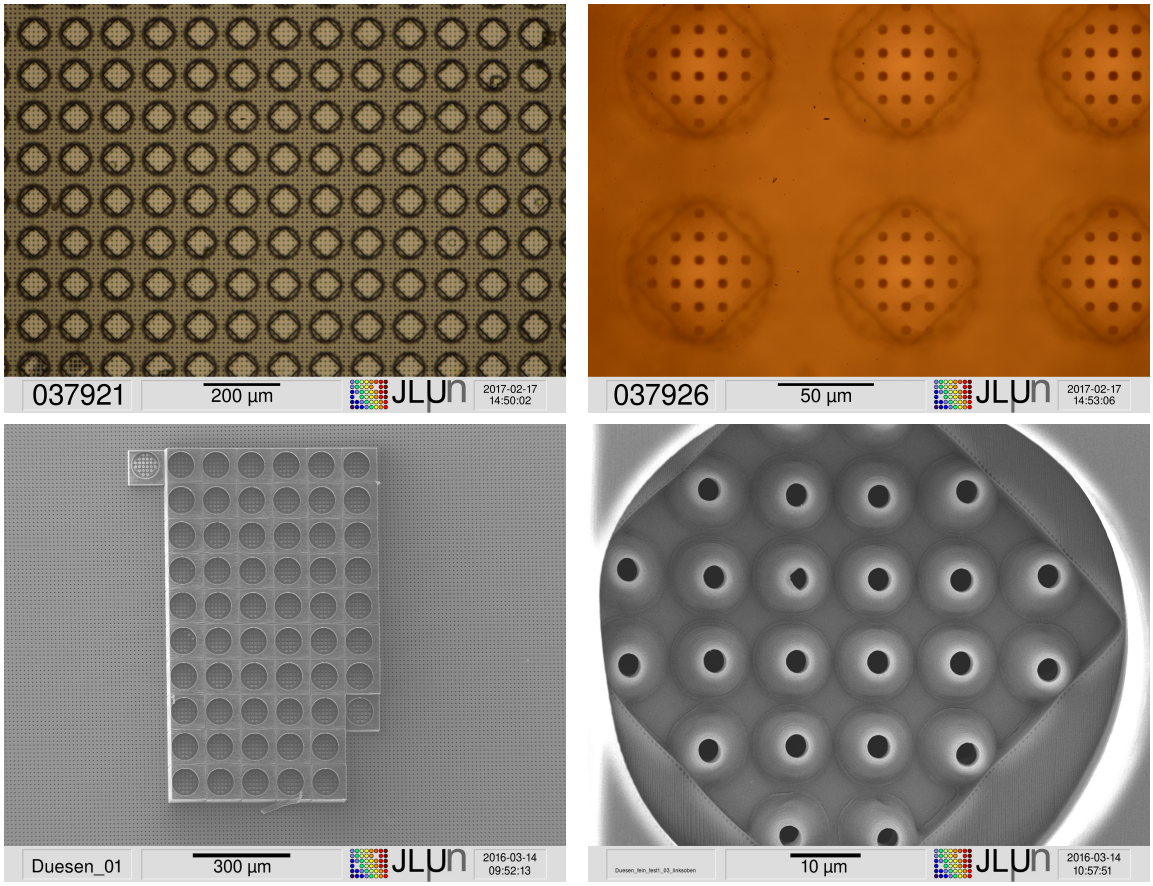

Figure 8. Top row: Two layer stacked photolithography of SU-8 layers on a macroporous silicon substrate (optical microscope images). Bottom row: SEM images of 3D microlithography on a macroporous silicon substrate with a pore pitch of 12 µm. The Nanoscribe-written structures include a square-shaped masking layer exposing groups of 24 pores, individual volcanoes aligned to these 24 pores, and a spacer and extraction electrode support layer with a circular opening for each group of emitters.

III. Conclusion

The fabrication of electrospray emitters by photolithography of photostructurable polymers is an interesting alternative to a classical pure silicon technology pathway, offering more freedom of design, especially in the third dimension, and potentially lower cost for design iterations during the research and development phase. Many important issues remain to be solved, such as the question of stability of the polymers under harsh space conditions, or the details of the integration with metallic extraction electrodes and ion optics for acceleration. So far, no show-stoppers for the application as scalable thrusters for small satellites or high precision missions have been identified.

Acknowledgments

Justus Liebig University gratefully acknowledge financial support by the German Federal Ministry for Economic Affairs and Energy under contract 50RS1604. We acknowledge the Karlsruhe Nano Micro Facility (KNMF, www.kit.edu/knmf) at the Karlsruhe Institute of Technology as well as the Beijing Key Laboratory for Metamaterials and Devices at Capital Normal University Beijing for providing access to 3D microlithography instrumentation at their respective laboratories. The authors thank Lin Ju of Justus Liebig University for the design of and for assistance with the amplifier electronics and Viktoryia Vatuliak of the Micro- and Nanofabrication Laboratory at the Centre for Materials Research ZfM/LaMa of Justus Liebig University for assistance in sample preparation.

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