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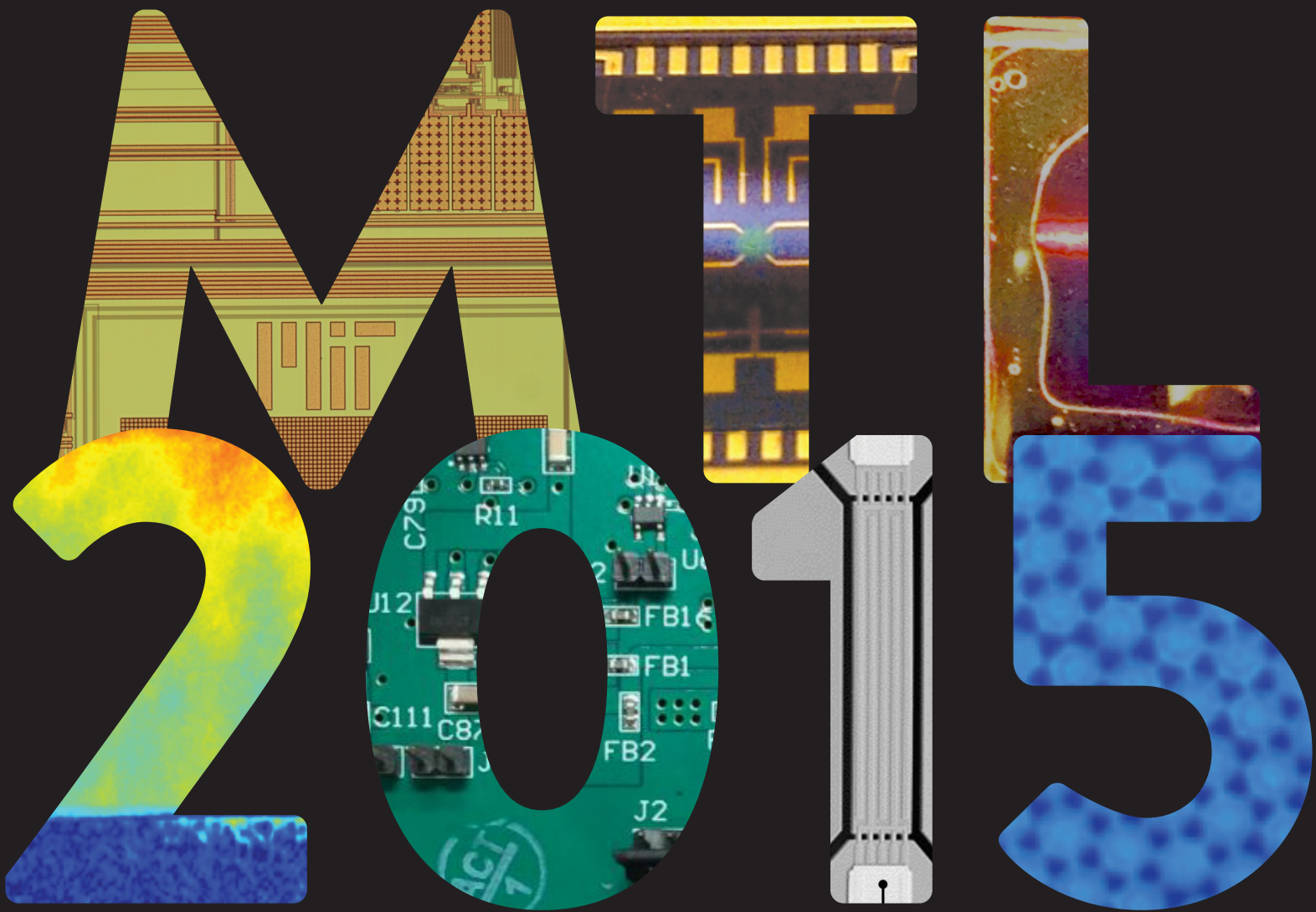
ANNUAL RESEARCH REPORT 2015

MASSACHUSETTS INSTITUTE OF TECHNOLOGY



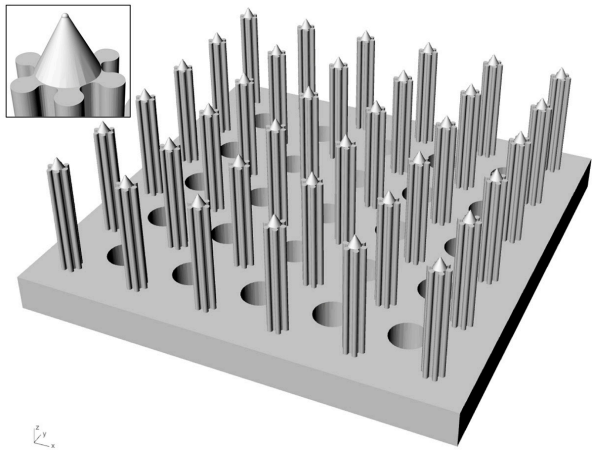
Additive Manufacturing of Three-Dimensional Microfluidics

L. F. Velásquez-García
Sponsorship: DARPA

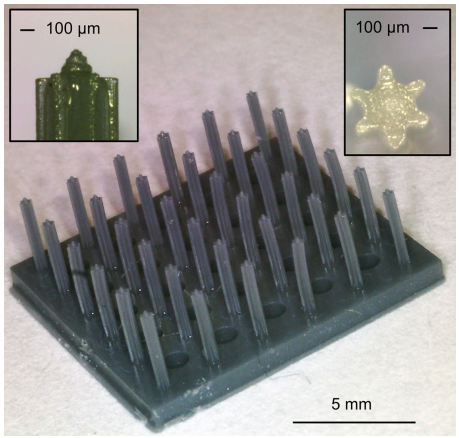
In many cases, microfluidics are manufactured in cleanrooms using semiconductor industry processes and materials, making them fairly expensive to produce. In addition, the device architecture is often a compromise between what should be made based on modeling and what can be made based on the planarity and thickness/depth limitation of most microfabrication processes. Moreover, a change of any of the in-plane features of the design typically requires the fabrication of one or more new lithography masks, incurring substantial costs and time delays. A manufacturing technology that can circumvent these difficulties without sacrificing device performance would greatly extend the kind of devices that can be made and the kind of commercial applications beyond research, high-end products, and large-volume products that can satisfied by microfluidic chips.

Additive manufacturing is a group of layer-by-layer fabrication methods that use a computer file to generate solid objects. Additive manufacturing started as a visualization tool of passive, mesoscaled parts; however, given the recent improvements in the resolution capabilities and cost of commercial 3D printers, additive manufacturing has recently been explored as a fabrication technology that could address the complexity of certain microsystems, e.g., microfluidics.

We are exploring the use of stereolithography to manufacture freeform microfluidics with three-dimensional hydraulic networks with features (range of dimensions, aspect ratio, morphology) that would be very hard to make using standard microfabrication processing. Stereolithography is an additive fabrication process that uses a computer file (Figure 1) to manufacture structures based on spatially controlled solidification of a liquid resin by photo-polymerization. For example, we have developed fabrication process flows for the creation of three-dimensional structures that can be used as multiplexed, externally fed electrospray emitter arrays (Figure 2); these structures have a minimum feature size and emitter density comparable to reported single-crystal silicon multiplexed electrospray devices. Current work focuses on exploring the resolution limits and capabilities of the 3D printing process, as well as in demonstrating working microfluidic chips.



▲Figure 1: Computer-aided design file of a monolithic array of 36 micro-sharpened, high aspect-ratio columns with lateral striations on top of a perforated plate and close-up of the side view of a tip.



▲Figure 2: A monolithic array of 36 3D-printed, micro-sharpened, high aspect-ratio columns with lateral striations on top of a perforated plate with close-up of the side view of a tip and top view of one of the columns. The structure could be used as a multiplexed externally fed electrospray source.

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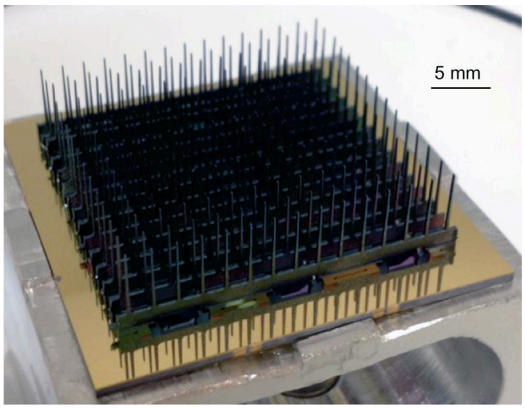
High-Throughput Manufacturing of Nanofibers using Planar Arrays of Microfabricated Externally Fed Emitters

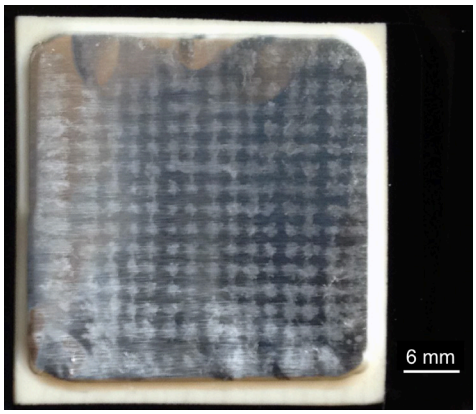
P. J. Ponce de Leon, F. A. Hill, L. F. Velásquez-García
Sponsorship: DARPA

Electrohydrodynamic jetting occurs when a strong electric field is applied to the free surface of a conductive liquid; the process can uniformly produce ion plumes, fine aerosol droplets, or continuous fibers with submicron diameters, i.e., nanofibers, depending on the properties of the liquid used and the ionization conditions. Nanofabrication via electrohydrodynamic jetting has received attention as a promising candidate for production of nanostructures because of its ability to create nano-thick films of high quality at lower temperature than standard solid-state processing. A key advantage of electrospinning, i.e., electrohydrodynamic jetting of nanofibers, over other fiber generation methods is its versatility in producing fibers of arbitrary length from a range of materials including polymers, metals, ceramics, and semiconductors. The applications of electrospun nanofibers include dye-sensitized solar cells, scaffolds for tissue engineering, electrodes for ultracapacitors, and separation membranes.

We created a technology for high-throughput generation of polymer nanofibers using planar arrays of microfabricated externally fed electrospinning emitters. Devices with emitter density as high as 25 emitters/cm^2 (Figure 1) deposit uniform imprints comprising fibers with diameters on the order of a few hundred nanometers using solutions of dissolved polyethylene oxide in water and ethanol as working fluid (Figure 2). We measured mass flux rates as high as 417 g/hr/m^2, i.e., 4x the reported production rate of leading commercial free-surface electrospinning sources. Throughput increases with increasing array size at constant emitter density, showing that the design can be scaled up with no loss of productivity. The largest measured mass flux resulted from arrays with larger emitter separation operating at larger bias voltages, indicating the strong influence of electrical field enhancement on the performance of the devices. Inclusion of a ground electrode surrounding the array tips helps control the spread of the imprints over large distances.



▲ Figure 1: An array of 15×15 externally fed electrospinning emitters (25 emitters/cm^2). From P. Ponce de Leon et al., Nanotechnology, vol. 26, no. 22, 225301 (10 pp.), June 2015.



▲ Figure 2: Collector imprints from an array of 225 emitters (25 emitters/cm^2). From P. Ponce de Leon et al., Nanotechnology, vol. 26, no. 22, 225301 (10 pp.), June 2015.

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- Ponce de Leon, F. A. Hill, E. V. Heubel, and L. F. Velásquez-García, "High-Throughput Manufacturing of Polymer Nanofibers via Electrohydrodynamic Jetting from Planar Arrays of Microfabricated Externally-Fed Emitters," presented at the *18th International Conference on Solid-State Sensors, Actuators, and Microsystems (Transducers 2015)*, Anchorage AK, June 2015.
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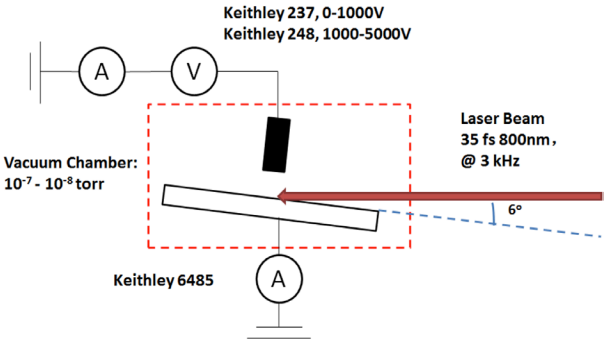
Optimization of the Morphology of Arrays of Nano-Sharp, Photon-Triggered Silicon Field Emitters to Maximize their Total Current Emission

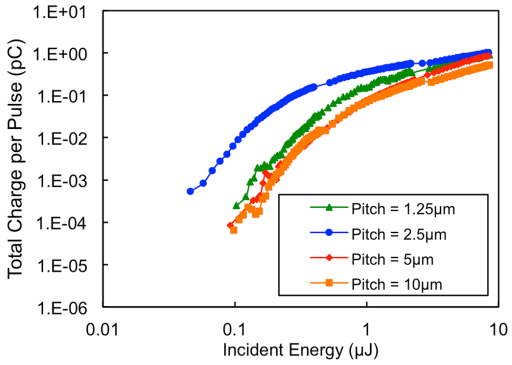
C. D. Dong, M. E. Swanwick, P. D. Keathley, F. X. Kärtner, L. F. Velásquez-García
Sponsorship: DARPA

Femtosecond ultrabright cathodes with spatially structured emission are a critical technology for applications such as free-electron lasers, tabletop coherent x-ray sources, and ultrafast imaging. State-of-the-art UV photocathodes have several disadvantages: (i) they need to be fabricated, stored, and operated in ultra-high vacuum and (ii) producing high current pulses reduces their lifetime due to the rapid degradation of the low workfunction material. Cathodes based on photon-triggered field emission, i.e., tunneling of electrons due to the interaction of high-intensity optical pulses with field enhancing structures, are a promising technology to bypass these shortcomings. We recently reported batch-fabricated photon-triggered field emission cathodes composed of massively multiplexed arrays of nano-sharp high-aspect-ratio silicon pillars; the devices are made using standard complementary metal-oxide semiconductor batch fabrication processes, are stored at atmospheric conditions, and can be operated at lower vacuum levels than standard photocathodes with no degradation. The devices are capable of pC-level emission with multi-kHz repetition, greatly increasing the total emitted charge per pulse compared to single-emitter sources. Through experiment and simulations, this work explores the optimization of the total electron yield of ultrafast photon-triggered field emission cathodes composed of arrays of nanosharp, high-aspect-ratio, single-crystal silicon pillars by varying the emitter pitch and height.

Arrays of 6-nm-tip-radius silicon emitters with emitter densities between 1.2 and 73.9 million tips.cm^{-2} and emitter height between 2.0 μm and 8.5 μm were characterized using 35-fs 800-nm laser pulses (Figure 1). Of the devices tested, the arrays with emitter pitch equal to 2.5 μm produced the highest total electron yield; arrays with larger emitter pitch suffer area sub-utilization; and in devices with smaller emitter pitch, the larger emitter density does not compensate for the smaller per-emitter current due to the electric field shadowing that results from the proximity of the adjacent tips (Figure 2). Experimental data and simulations suggest that 2-μm-tall emitters achieve practical optimal performance as shorter emitters have visibly smaller field factors due to the proximity of the emitter tip to the substrate, and taller emitters show marginal improvement in the electron yield at the expense of greater fabrication difficulty.



▲Figure 1: Schematic of the experimental apparatus used to characterize the photon-triggered silicon field emitter arrays.



▲Figure 2: Total emitted charge per pulse vs. incident laser pulse energy for devices with emitter pitch equal to 1.25 μm, 2.5 μm, 5 μm, and 10 μm and emitter height equal to 8.5 μm. From C. Dong et al., Nanotechnology, vol. 26, no. 26, 265202 (11pp), 2015.

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- M. Swanwick, P. D. Keathley, A. Fallahi, P. R. Krogen, G. Laurent, F. X. Kärtner, and L. F. Velásquez-García, "Nanostructured Ultrafast Silicon-Tip Optical Field Emitter Arrays," *Nano Letters*, vol. 14, no. 9, pp. 5035-5043, Jul. 2014.
- P. D. Keithley, A. Sell, W. P. Putnam, S. Guerrera, L. F. Velásquez-García, and F. X. Kärtner, "Strong-Field Photo-Emission From Silicon Field Emitter Arrays," *Annalen Der Physik*, vol. 525, nos. 1-2, pp. 144-150, Feb. 2013.
- C. Dong, M. E. Swanwick, D. Keithley, F. X. Kärtner, and L. F. Velásquez-García, "Multiplexing and Scaling-Down of Nanostructured, Photon-Triggered Silicon Field Emitter Arrays for Maximum Total Electron Yield," *Nanotechnology*, vol. 26, no. 26, 265202 (11pp), Jun. 2015.

Advanced X-Ray Sources for Absorption Imaging of Low-Z Materials

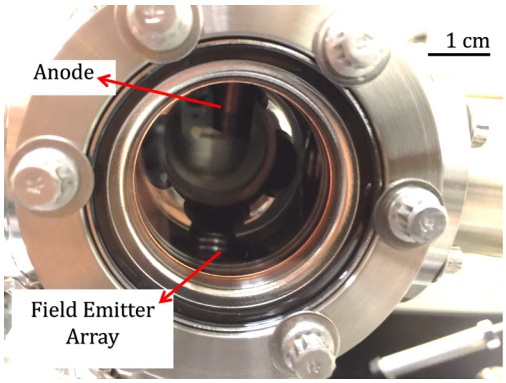
A. Basu, M. E. Swanwick, A. A. Fomani, L. F. Velásquez-García
Sponsorship: DARPA

X-rays are widely used in applications such as healthcare, airport security, crystallography, spectroscopy, and microfabrication. The development of miniaturized X-ray sources could satisfy applications where the target areas are small or where the smaller dimensions and lighter weight of the X-ray source enable desirable capabilities such as portability. For example, compact X-ray sources can revolutionize computerized tomography (CT) by making possible the implementation of a system with multiple X-ray sources that provides a wide range of information without the need to implement a rotating gantry.

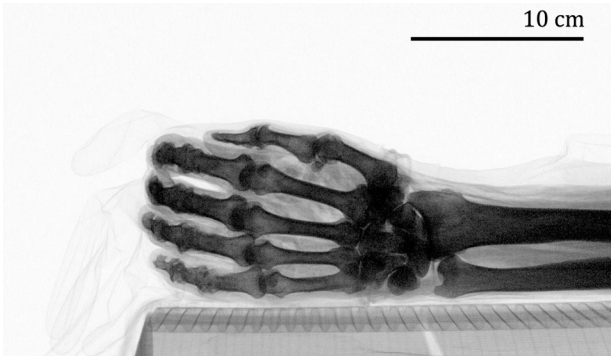
A field emission cathode is an attractive alternative to a conventional thermionic cathode as an electron source in a portable X-ray source because of the lower vacuum it requires to operate, its faster response, and its resilience to traces of reactive gases. Field emission cathodes use high-surface electric fields on the emitter tip surface to narrow the potential barrier that traps electrons in the material, allowing electrons to quantum tunnel into vacuum. Miniaturization and multiplexing of field emitters result in nanostructured field-emitter arrays capable of high-current emission at a low (< 150 V) voltage. The field emitters used in our X-ray source are capable of generating mA-level dc currents even when operated continuously for many hours. High-current cathodes make it possible to capture images in a short time, which helps to reduce any blurriness of the image due to movement of the sample.

X-rays generated from a target anode can be categorized as either bremsstrahlung or fluorescent. On the one hand, bremsstrahlung X-rays span the entire energy range of the bombarding electrons with the maximum energy being determined by the voltage applied to the anode. On the other hand, fluorescent X-rays are characteristic of the target material and appear as specific sharp peaks in the X-ray spectrum. While bremsstrahlung X-rays give rise to low-contrast polychromatic images, fluorescent X-rays could be used to produce quasi-monochromatic, high-contrast images.

For over four years our group has developed advanced field-emission-enabled, near-monochromatic X-ray sources capable of imaging soft tissue structures. Our latest development is a portable X-ray source (200 cm^3 chamber size) with a reflection anode composed of a copper rod coated with a molybdenum thin film and a field emission cathode (Figure 1). A 25 l/s portable ion pump keeps the chamber base pressure at approximately 10^{-8} Torr. At an anode bias voltage of 35 kV, the X-ray source maximizes the percentage of photons with 17.8 keV, which corresponds to the Kα peak of Mo; these X-rays are energetic enough to go through air without significant attenuation (~95% transmission) but are of low-enough energy to generate high-contrast absorption images when interacting with soft tissue. Using the X-ray source, we obtained absorption images of ex-vivo samples captured on a CsI scintillator operated in fluoroscopic mode (Figure 2). Features as low as 160 µm were visible in the images.



▲Figure 1: The inside of the X-ray chamber as seen through a glass port. The field emitter array is hidden from view



▲Figure 2: Absorption X-ray image of ex vivo human hand captured with anode bias voltage equal to 35 kV and cathode current of 250 µA for 60 seconds of exposure time.

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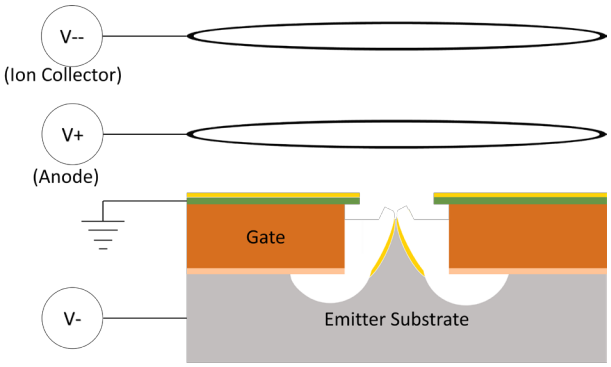
- A. Basu, M. Swanwick, A. Fomani, and L. Velásquez-García, "A Portable X-Ray Source With a Nanostructured Pt-coated Silicon Field Emission Cathode For Absorption Imaging of Low-Z Materials," *Journal of Physics D: Applied Physics*, vol. 48, pp. 225501, 2015.

A Field Emission-Based Ultra-High Vacuum Pump for Cold-Atom Interferometry Systems

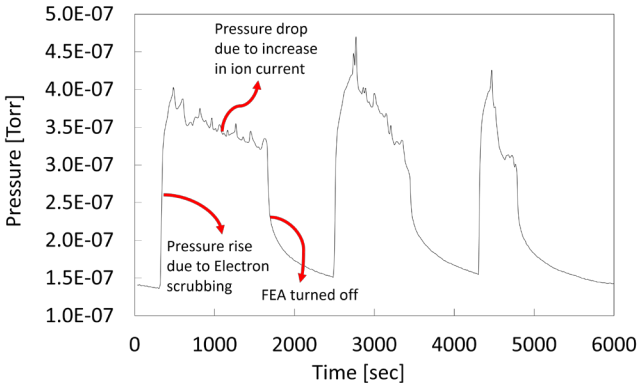
A. Basu, M. A. Perez (ColdQuanta, Inc.), L. F. Velásquez-García
Sponsorship: DARPA

The discovery of magneto-optical trapping of alkali metal vapors in the late 1980s generated a strong interest in developing miniaturized atomic clocks and sensors based on cold alkali atom interferometry. Chip-scale, high-precision atomic sensors can be used in a great variety of exciting applications including fundamental scientific discovery (e.g., general relativity and geophysics), inertial navigation (e.g., gyroscopes and accelerometers), and geological survey (e.g., magnetometers and gravimeters). Cold-atom interferometry needs ultra-high vacuum (UHV, pressure < 10^{-9} Torr) to operate; therefore, portable cold-atom sensors require miniaturized UHV pump technology compatible with alkali vapor that operates at low power. Standard UHV ion pumps, which use high magnetic fields to increase the ionization probability, are not ideal to maintain vacuum in a chip-scale atomic sensor because the intensity of the magnetic field increases with the reduction in size of the pump and because the magnetic field of the pump can alter the quantum states of the laser-cooled atoms, leading to incorrect measurements. A better alternative is to use an electron source to provide a surplus of electrons to increase the ionization probability, eliminating the need for a magnetic field. A field emission electron source is a good choice for that because, unlike state-of-the-art thermionic cathodes, they do not require high temperature to operate, which makes them compatible with the reactive alkali environment inside atomic vapor cells.

We preliminarily demonstrated a magnetic-less ion pump design (Figure 1) that uses field electron emission to create a self-sustained plasma within a 200 cm^3 vacuum chamber. A silicon-based, nanostructured, self-aligned, gated field emitter array (FEA) is used as electron source. Two electrodes, both consisting of structural rings wrapped with titanium wire, are placed above the FEA and biased at voltages that enable collection of either electrons or ions. The ion collector is the getter of the pump, capturing the ions both physically (bombardment) and chemically (chemisorption). The apparatus has a rubidium dispenser for releasing the alkali metal vapor inside the chamber, and the chamber is connected to an external pump system capable of maintaining a base pressure of ~10^{-8} Torr within the chamber. The performance of the field emission cathode did not deteriorate due to the presence of Rb at pressures as high as 7×10^{-6} Torr. The pump performance is shown in Figure 2. An initial rise in pressure (due to electron scrubbing) was followed by a 25% drop in pressure (from 4.0×10^{-7} Torr to 3.0×10^{-7} Torr) when the ion current was increased from 0 to 0.5 nA (by increasing the bias on the negatively charged ion collector). Current work focuses on the optimization of the electron impact ionization process to improve pumping performance.



▲ Figure 1: Schematic of the pump architecture. The FEA is represented by a single emitter tip; the anode and ion collectors are ring-shaped structures.



▲ Figure 2: Chamber pressure vs. time. From "Nanostructured Silicon Field Emitter Array-Based High-Vacuum Magnetic-Less Ion Pump for Miniaturized Atomic Spectroscopy Sensors," *Transducers 2015*, Anchorage AK, June 2015.

FURTHER READING

- A. Basu, M. A. Perez, and L. F. Velásquez-García, "Nanostructured Silicon Field Emitter Array-Based High-Vacuum Magnetic-Less Ion Pump For Miniaturized Atomic Spectroscopy Sensors," 18th International Conference on Solid-State Sensors, Actuators and Microsystems (Transducers 2015), Anchorage AK, June 2015.

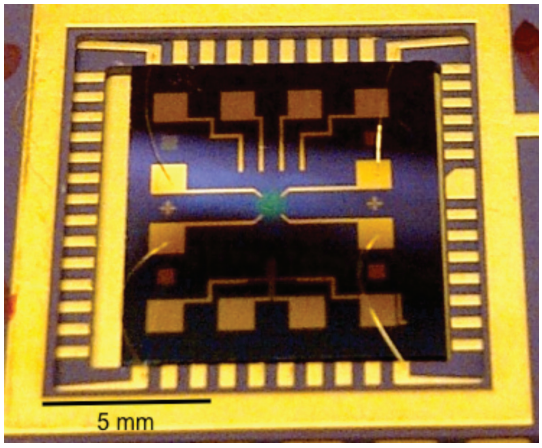
Electrospray-Printed 2D Material Humidity Sensors

A. P. Taylor, L. F. Velásquez-García
Sponsorship: Edwards Vacuum

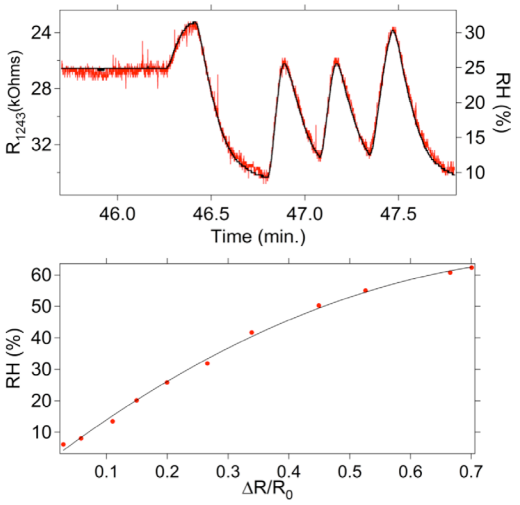
State-of-the-art conductometric gas sensors, based on semiconducting metal oxide films (MOXs), are widely used due to their simplicity and broad applicability to detect many species. However, only a few MOXs show an adequate combination of catalytic activity and thermodynamic stability for gas sensing; these MOXs need to be doped with noble metal nanoparticles to compensate for their poor gas sensitivity, which visibly increases their cost. Fabrication via electrohydrodynamic jetting has recently received attention as a promising candidate for production of low-cost micro- and nanosystems because of its capability to create thin films of high quality without the extreme conditions of standard semiconductor processing (i.e., high vacuum and/or high temperature).

An attractive substitute active material for chemical gas sensing is graphene oxide (GO) because of its high sensitivity to surface adsorbates and compatibility to harsh environments. Thin-film GO sensors have been fabricated with aqueous suspensions of GO flakes using drop casting, air-brush spraying, spin coating, and inkjet printing. Nonetheless, electrospray printing of GO thin-film sensors offers more precise control of the film properties than the other techniques and can also lower production costs through emitter multiplexing. We manufactured GO sensors at low temperatures (< 100 ˚C) with average layer thickness around 60 nm and characterized their response to humidity in an environmental chamber.

We fabricated devices with multiple electrode configurations on SiO_2-coated Si wafers using contact photolithography and the lift-off technique, and electrosprayed a thin film of GO through a shadow mask onto the electrode structures to form the sensors. We then gold wire-bonded the completed sensor chips into standard IC packages (Figure 1) and placed our GO sensors along with a commercially available humidity sensor (Honeywell HIH-4000) inside an environmental chamber and varied the humidity. A data logger recorded the change in resistance of the GO sensor (Figure 2 top, red curve) and the response of the commercial sensor (Figure 2 top, black curve); the two data sets tracked each other closely. The change in humidity shows a quadratic behavior with the change in resistance of the GO sensor (Figure 2 bottom) where $\Delta R/R_0=(R_{1243}-R_0)/R_0$ and R_0=39kΩ. The results were reproducible on different days, and the GO sensors showed no signs of degradation after storage for more than one month.



▲Figure 1: Electrospray-printed GO sensor (greenish dot at center) on top of Au electrodes in the Van der Pauw configuration.



▲Figure 2: GO sensor response to humidity (red) compared with a commercially available sensor (top) and relative humidity as a function of the sensor response (bottom).

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MEMS and NEMS for space, energy, healthcare, manufacturing, and analytical applications. High-electric field phenomena, e.g., electrospray, field emission, X-rays. Nanosatellite propulsion.

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SELECTED PUBLICATIONS

M. E. Swanwick, C. D. Dong, P. D. Keathley, A. Fallahi, F. X. Kärtner, and L. F. Velásquez-García, "Pitch scaling of ultrafast, optically-triggered silicon field emitter arrays," *Technical Digest of the 27th International Vacuum Nanoelectronics Conference (IVNC 2014)*, Engelberg, Switzerland, pp. 69 -70, July 6–10, 2014.

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