A PECVD CNT-BASED OPEN ARCHITECTURE FIELD IONIZER FOR PORTABLE MASS SPECTROMETRY

L.F. Velásquez-García[1], and A.I. Akinwande[1,2]
[1]Microsystems Technology Laboratories, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA
[2]Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA

ABSTRACT

This paper reports a novel carbon nanotube (CNT)-based field ionizer that is part of a portable micro gas analyzer. The device uses a micro-fabricated 3D foam-like silicon structure (μfoam) to increase the neutral particle flux, resulting in higher ion current. The μfoam is fabricated using deep reactive ion etching (DRIE). The ionizer uses plasma enhanced chemical vapor deposited (PECVD) CNTs as field enhancers. The PECVD CNT growth interacts with the μfoam to produce a sparse array of isolated CNT clusters on top of the μfoam. Electrical tests of the device both as an electron field emitter and field ionizer are reported and discussed.

1. INTRODUCTION

The development of portable mass spectrometry technology has enjoyed an active research interest in the past decade. The motivation behind this effort is driven by the desire for rugged systems that are smaller, lighter, cheaper, faster, and more power efficient [1-3]. Portable mass spectrometers require low power and compact gas ionizers. An option could be to use electron impact ionizers (EIIs), where a stream of electrons is used to ionize neutral molecules by collision. EIIs based on thermionic emission [4] are not ideal for portable mass spectrometry because they consume high power (>1 W) and cannot work at high pressures because of reliability problems due to back-ion bombardment.

EIIs can also use field-emitted electron sources. In this case, the ionizer has a field enhancer (tip) that is biased negative with respect to a gate. The presence of a local high field surrounding the tip allows electrons to tunnel out of the tip to vacuum, in a process described by the Fowler-Nordheim model [5]. A second gate, biased at a lower potential than the tip can be use to avoid back-ion bombardment (Fig. 1).

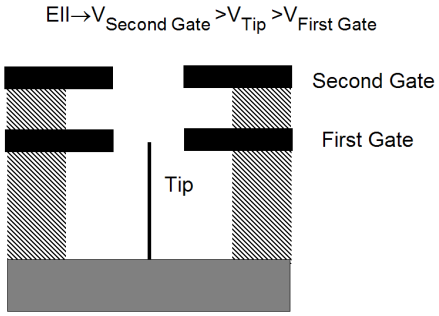

Figure 1: Schematic of electron impact ionizer.

EIIs based on electron field emission are more attractive because they are more power efficient than thermionic ionizers and because can work at higher pressures. Field emission EIIs have been demonstrated, in particular using double-gated PECVD CNT structures [6].

EIIs inherently produce fragmentation of the analyte, thus posing complications in its identification. This is particularly important for the identification of complex bio-molecules. Field ionizers (FIs) can be used to obviate this problem. FIs also use field enhancers to ionize, but in this case the tip is biased positive with respect to the gate resulting in a different physical process. If the local electric field at the tip is strong enough, an electron in the outer shell of a neutral molecule drifting-by can tunnel to the tip, effectively ionizing the molecule [5]. This ionization process produces substantially less fragmentation of the analyte than electron impact ionization and does not consume high power. However, state of the art field ionizers require typically 5 – 10 kV and also need high vacuum [7]. The requirement of high voltage implies complex electronics while the requirement for high vacuum implies high pump power. PECVD CNT NEMS FIs suitable for portable mass spectrometry have been reported [8], but their net output current is very small due to restrictions in the molecular flux reaching the tips because of the constraints imposed by a closed architecture. In an open architecture (Fig. 2) this problem is circumvented.

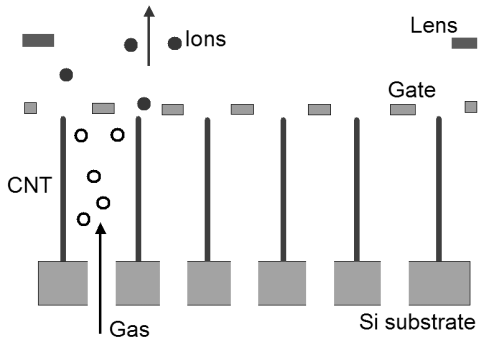

Figure 2: An open architecture field ionizer. The field enhancers lie on top of a perforated structure to maximize analyte flowrate near the strong field zone.

2. DESIGN AND FABRICATION

There are two key design considerations for making field ionizers: (a) the tip electrostatic field for narrowing the barrier to electron tunneling and (b) the neutral molecule flux reaching the tips to increase the supply of species to ionize. In general, field ionization requires substantially larger electric

fields than electron field emission because the ionization potential of gases (~15 eV) is about three times larger than the workfunction of metals (~4.8 eV). Therefore, it is desirable to have tips with a very large field factor to reduce the bias voltage needed. The voltage reduction could also reduce the complexity of the drive circuitry and improve the long-term reliability of the ionizer. An effective way to obtain large field factors is to use very high aspect ratio structures with enough spacing in between to avoid shadowing. The best field enhancers are whisker-like structures [9]. PECVD CNTs are very attractive as field enhancers because of their very large aspect ratio and diameters of the order of a few nanometers [10]. CNTs are also high-performance mechanical structures that are chemically resistant. Isolated PECVD CNTs are typically grown by defining the catalyst pads down to sizes below 200 nm using electron beam lithography [10]. However, electron beam lithography is a low-throughput and expensive processing technique.

A second consideration to make FIs is the neutral species molecular flux reaching the tip. The neutral molecules have to be close enough to the tip to be immersed in a region of high electric field that can result in tunneling of one of its outer-shell electrons to the tip. For high enough electric fields the ionization process is transport limited. Close ionizer architectures such as in [6], where the gates are limiting the line-of-sight of incoming neutral molecules, severely restrict the molecular flux and hence produce smaller ion currents.

The device reported in this document uses a 3D foam-like silicon structure (the μfoam, Fig. 3) to achieve both neutral flux augmentation and sparse PECVD CNT growth. The μfoam gives high accessibility to the incoming neutrals to reach the field enhancers and thus increase the ion current. The μfoam interacts with the plasma to reduce the available growth area, effectively spacing the growth sites (Fig.4). Also, we speculate that the front area of the μfoam makes it possible to coalesce isolated dots from the field-deposited catalyst and hence have isolated CNT growth within each growth site. The CNTs produced with this method are 5- 10 μm tall with about 70 nm of average tip diameter (Fig. 5).

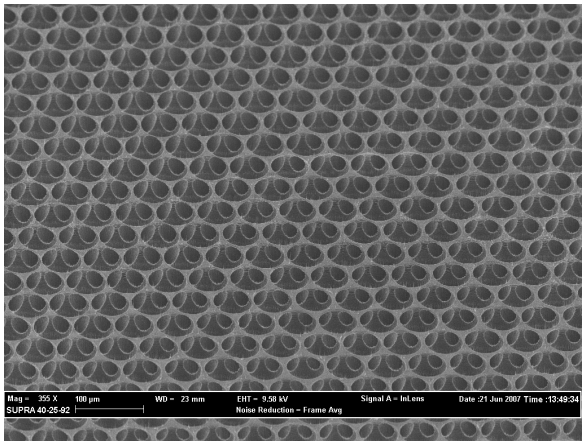

Figure 3: Tilted top view of the 3D μfoam.

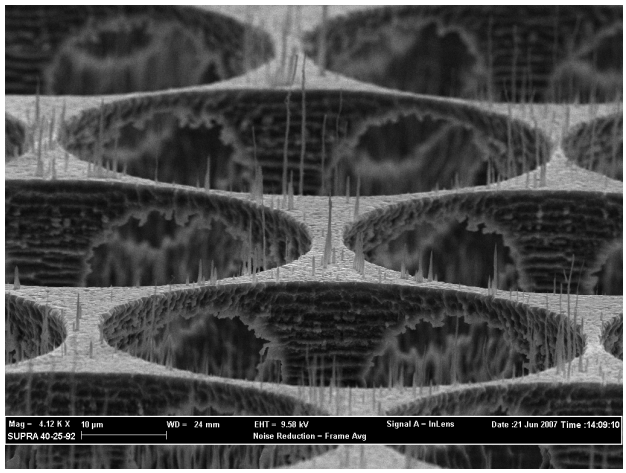

Figure 4: Detail of sparse PECVD CNT cluster on the μfoam.

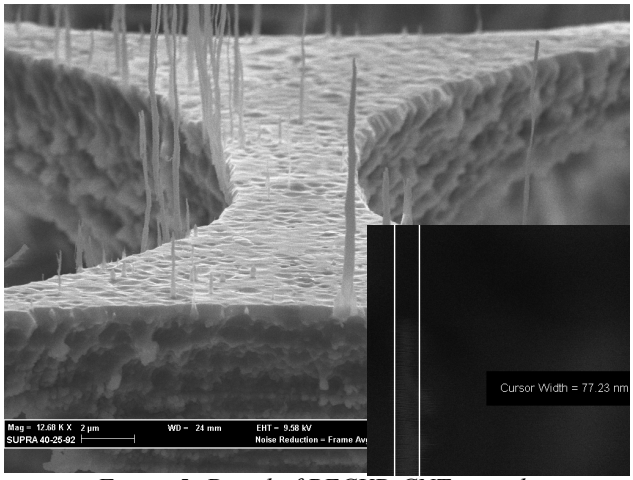

Figure 5: Detail of PECVD CNT growth.

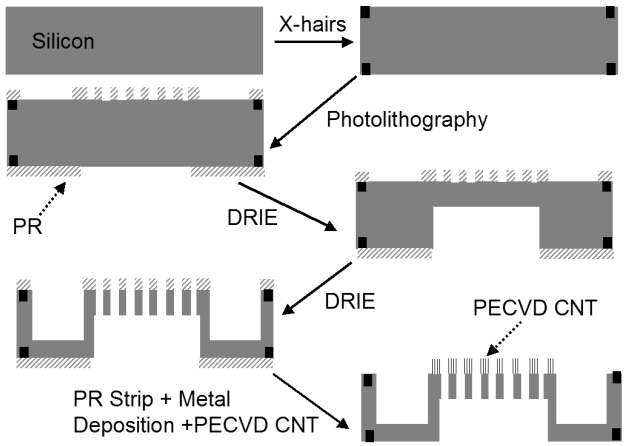

Figure 6: Schematic of process flow.

The fabrication of the devices uses 6-inch n-Si wafers (Fig. 6). The process starts with the definition of cross hairs on both surfaces of the substrate. Then, contact photolithography is conducted on both surfaces on a 10 μm-thick spun coated photoresist (PR) film. The PR film on the top surface is used to define the μfoam and field enhancement region, while the PR film on the bottom surface is used to define the recesses for reducing the thickness of the μfoam. The top surface also

has the features that are used to die-saw the devices. The substrate is then etched using a DRIE step. The wafer is flipped over, and etched with a series of DRIE and reactive ion etching (RIE) steps to carve the μfoam and give it three-dimensionality. The PR films are then stripped using piranha. A 7 nm-thick e-beam evaporated Ni film is then deposited on the top surface of the μfoam using a shadow mask. The Ni film is reduced in ammonia at 650°C and 1.5 Torr of chamber pressure. PECVD CNTs are grown in a reactor at 825°C and 5 Torr that uses a 4:1 ammonia and acetylene mix [10].

3. EXPERIMENTAL RESULTS

Figure 7 shows the IV characteristics of the device tested as electron field emitter in vacuum better than 10^{-9} Torr. A schematic of the testing rig is shown in Fig. 8. A turn-on voltage of 75 V and maximum current of 1.4 mA @ 260 V were measured. Linearity between the gate and collector currents was verified to discard the possibility that the gate current is emanated from leakage through the dielectric instead of field emission (Fig. 9).

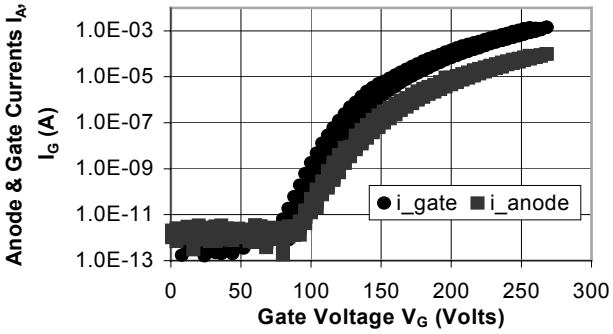

Figure 7: IV characteristics of the device as field emitter.

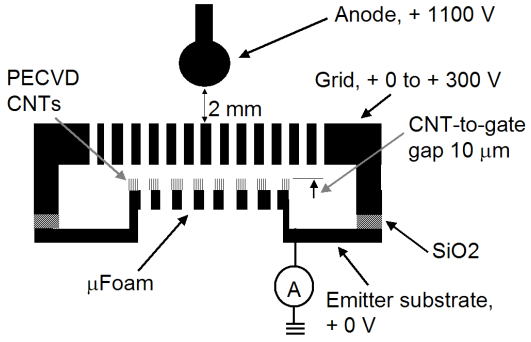

Figure 8: Schematic of the triode setup used for testing. The gate is a DRIE-patterned grid. The collector is a 2 mm diameter ball in front of the device.

The field emission data is in agreement with the Fowler Nordheim (FN) model (Fig. 10) [5]. However, the slope of the curve in the FN plot is reduced for large enough currents. This behavior suggests resistive ballasting by the μfoam, a desirable attribute for uniform field emission arrays. We speculate that the high surface-to-volume structure of the μfoam limits the current the same way very high aspect ratio silicon columns do [11].

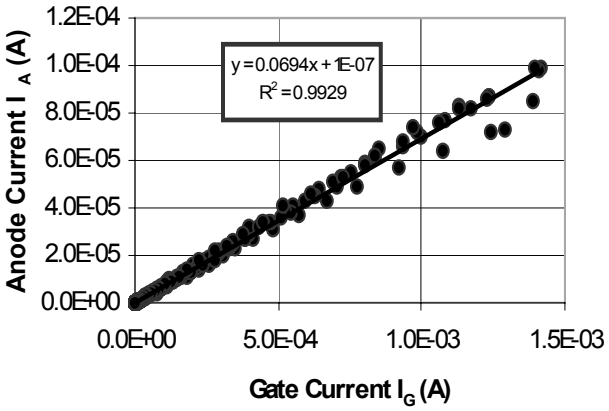

Figure 9: Anode Current vs. Gate Current.

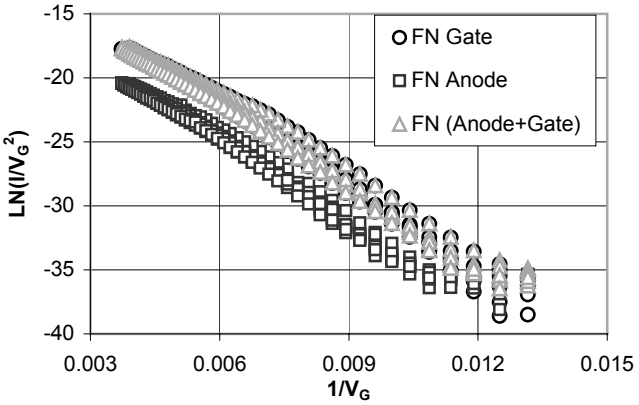

Figure 10: Fowler Nordheim plot

Analysis of the data suggests a field factor β of 3.7×10^5/cm. If the functional dependence of the field factor with respect to the emitter tip radius r is assumed as

$$\beta \approx 1/r \qquad (1)$$

then for the workfunction of graphite (4.8 eV) the tip radius is about 32 nm, in good agreement with the SEM metrology.

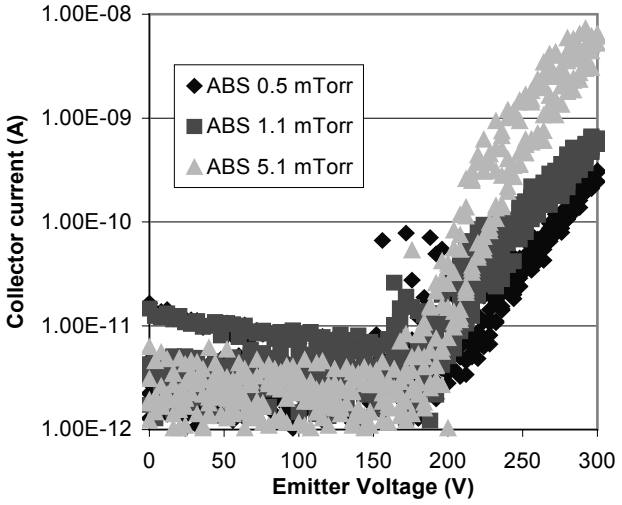

Figure 11: IV characteristics of the device as a field ionizer.

Figure 11 shows the collector (ball) current vs. emitter voltage when the device is used as a field ionizer. Three Argon chamber pressures where used in the test: 0.5, 1.1, and 5.1 mTorr. The collector was biased at –1100 V in all the tests. In this configuration, the device has a turn-on voltage of 180 V and a maximum ion current of 7.3 nA @ 300 V for the 5.3 mTorr case. There is a linear dependence between the gate and collector currents where the gate current is 5000 times larger.

A semilog plot of the collector current vs. the inverse of emitter voltage for the three pressure cases (Fig. 12) shows that the slopes of the three data sets are to first order the same. Also, the linearity between the gate and collector currents in each data set demonstrates that the data comes from a field process. We believe that the ion current is mainly due to field ionization because the distances between the collector, gate and CNTs are not large enough to produce electron impact ionization at the working pressure. A distance of a few times the mean free path λ is required and for 1 mTorr the mean free path is about 5 cm.

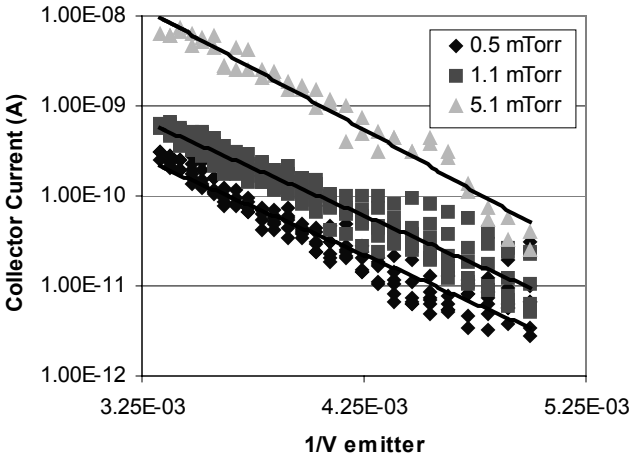

Figure 12: Semilog plot of field emission IV characteristics (collector current).

4. CONCLUSIONS

A novel carbon nanotube (CNT)-based field ionizer is reported. The device uses a μfoam structure to enhance the neutral particle flux and achieve sparse clusters of high aspect ratio PECVD CNTs from a field-deposited catalyst, without complex processing such as electron beam lithography. Tests of the device as a field emitter demonstrate electron emission in agreement with FN model. Resistive ballasting from the μfoam is suggested by these experiments. Tests of the device as a field ionizer show linear pressure dependence and constant slope in a semilog diagram, suggesting a barrier process. The experimental conditions of the ionization tests suggest field ionization as the likely physical ionization process.

5. ACKNOWLEDGEMENTS

The authors would like to thank the staff of the MIT's Microsystems Technology Laboratories (MTL) for their help in the fabrication of the devices. The work reported in the paper was sponsored by DARPA/MTO and the US Army Soldier Systems Center (Natick, MA) through contracts # W911QY-05-1-0002 (DARPA program manager Dennis Polla, and Army program manager Henry Girolamo).

6. REFERENCES

[1] B. Ghodsian, M. Parameswaran, and M. Syrzycki, "Gas Detector with Low-Cost Micromachined Field Ionization Tips", *IEEE Electron Dev. Lett.*, 1998, vol 19, No. 7, pp. 241-243, 1998.

[2] S. C. Terry, J. H. Jerman, and J. B. Angell, "A Gas Chromatographic Air Analyzer Fabricated in a Silicon Wafer", *IEEE Trans. Electr. Dev.,* vol 26, Issue 12, pp. 1880-1886, 1979.

[3] R. R. Reston and E. S. Kolesar, "Silicon-Micromachined Gas Chromatography System Used to Separate and Detect Ammonia and Nitrogen Dioxide – Part I: Design, Fabrication, and Integration of the Gas Chromatography System, *J. Microelectromech. Syst.,* vol. 3, No. 4, pp. 134-146, 1994.

[4] K. T. Tompson, "Theory of Ionization by Cumulative Action of Successive Impacts by Electrons and by Quanta of Resonance Radiation", *Phys. Rev.,* vol 20, pp. 283-299, 1922.

[5] R. Gomer, *"Field Emission and Field Ionization",* AIP, New York, 1993.

[6] L.-Y. Chen, L. F. Velásquez-García, X. Wang et al, "Design, Fabrication and Characterization of Double-Gated Vertically Aligned Carbon Nanofiber Field Emitter Arrays", *Technical Digest of the 20th IVNC*, Chicago IL, USA, 2007, pp. 82-83.

[7] E. de Hoffmann and V. Stroobant, *"Mass Spectrometry: Principles and Applications",* John Wiley & Sons, West Sussex, England, 2002.

[8] L.-Y. Chen, L. F. Velásquez-García, X. Wang, K. B. Teo and A. I. Akinwande, "A Micro Ionizer for Portable Mass Spectrometers using Double-gated Isolated Vertically Aligned Carbon Nanofiber Arrays", to be presented in the 2007 IEEE International Electron Device Meeting, Washington DC, USA.

[9] T. Utsumi, "Vacuum microelectronics: What's new and exciting," *IEEE Transactions on Electron Devices*, Vol. 38, No. 10, 1991, pp. 2276-2283.

[10] K. B. K. Teo, S.-B. Lee, M. Chhowalla et al, "Plasma enhanced chemical vapour deposition carbon nanotubes/nanofibers –How uniform do they grow?", *Nanotechnology*, vol 14, pp. 204-211, 2003.

[11] L. F. Velásquez-García, B. Andeoti, Y. Niu and A. I. Akinwande, "Uniform High Current Field Emission of Electrons from Si and CNF FEAs individually controlled by Si Pillar Ungated FETs", to be presented in the 2007 *IEEE International Electron Device Meeting*, Washington DC, USA.