A Micro Ionizer for Portable Mass Spectrometers using Double-gated Isolated Vertically Aligned Carbon Nanofiber Arrays

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Abstract

We report micro-fabricated double-gated vertically aligned carbon nanofiber (CNF) arrays for ionization of gasses in low power portable mass spectrometers. The devices can be operated in one of two modes − electron impact ionization (EII) or field ionization (FI). When operated as electron impact ionizer, power dissipation was reduced from >1 W typical of thermionic emission based electron impact ionizers to <100 mW. When operated as a field ionizer, the turn-on voltage for field ionization is reduced from 5-10 kV typical of ungated ionizers to 350 V.

Introduction

Portable mass spectrometers require low power and compact gas ionizers. State of the art instruments use electron impact ionizers based on thermionic emission sources or ungated field ionizers [1,2]. Thermionic electron sources consume high power, typically >1 W and hence are not suitable as ionizers for portable mass spectrometers. On the other hand, field ionizers do not consume high power but require high voltages, typically 5-10 kV and also high vacuum. The requirement for high voltage implies complex electronics while the requirement for high vacuum implies high pump power. To address these issues, we developed micro-fabricated double-gated vertically aligned carbon nanofiber (VA-CNF) arrays which were utilized as electron impact ionizers and field ionizers.

EII is based on field emission of electrons and collision of the accelerated electrons with neutral gas molecules as shown in Figure 1. The double-gated CNF array is biased as a field emission electron source with the first gate as the extractor and the second gate as a focus. When the second gate is biased at the lowest potential, the CNFs are protected from back ion bombardment. The relationship of the ionization current ($I_I(E)$) to electron current ($I_E(E)$) is given by

$$\frac{I_I(E)}{I_E(E)} = \rho \times L \times \sigma_{Total}(E)$$

E is the energy of the electrons. ρ [cm^{-3}] is the number density of neutral molecules in the gas (pressure), L [cm] is the collision path length, and σ(E) [cm^2] is the total ionization cross section. The collision path length (L) is the distance between the electron source and the ion collector.

In field ionization, electrons tunnel from neutral molecules to the CNF tip due to high electrostatic field near the tip surface of the VA-CNF [3,4]. The double-gated carbon nano fiber array acts as a field ionizer when the CNF tip is biased to have the highest potential relative to the gates and the collector as shown in Figure 2. The potential barrier experienced by tunneling electron is shown in Figure 3 and it can be approximated as a trapezoidal barrier. Using the WKB approximation, the ion current is expressed as

$$I_i = q \times \left(\frac{P}{kT}\right) \times C \times \exp\left(-B \times \left(1 - \left(\frac{\phi}{I}\right)^{3/2}\right) \times \frac{I^{3/2}}{F} \times \alpha\right)$$

P is the pressure, T is the temperature, k is the Boltzmann constant, q is the electronic charge, I is the ionization potential of the molecule, ϕ is the CNF workfunction, C is a constant and F is the tip electrostatic field. B = 6.87 x 10^7 and α is the image force lowering term. Assuming a linear relationship between the tip field and the applied gate voltage, the ion current has a linear dependence on pressure and exponential dependence on voltage. Furthermore, there is minimal risk of ion bombardment of the tip. One advantage of field ionization over EII is that it reduces fragmentation of analytes typical of EII.

Ionizer Design and Fabrication

The ionizers were designed such that the electric field generated at the tip is maximized and the shielding effect from the neighbors is minimized while the device is capable of handling a large breakdown voltage. To fabricate the double-gated CNF structure, CNFs were first synthesized. E-beam lithography and lift-off technique were used to define a 250nm diameter and 4nm thick Ni catalyst at each emission site spaced 10μm apart. This catalyst size guarantees nucleation of a single Ni dot at each site and subsequent growth of an isolated 4μm tall VA-CNF using plasma enhanced chemical vapor deposition (PECVD) at 725°C, as shown in Fig. 4 [5].

Once CNF was synthesized, the extraction gate and the out-of-plane focus gate were fabricated with a novel photoresist (PR) planarization technique and the process flow is shown in Fig. 5. This fabrication process consists of: (1) Formation of the gate insulator and the gate electrode (step A through E). A conformal layer of plasma enhanced chemical vapor deposition (PECVD) oxide was deposited as the gate insulator to separate CNFs and the gate material (amorphous-Si), as shown in Fig 6 (a). Next, a conformal PECVD doped a-Si was deposited on top of the oxide to form a gate electrode (Fig 6 (b)). Steps C-E illustrate the self-aligned

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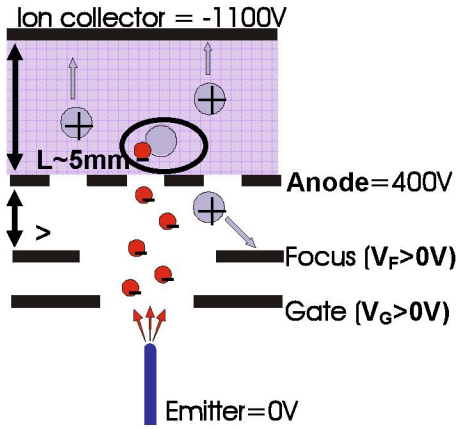

Figure 1. Double-gated VA-CNF operated as a field emitted electron impact ionizer (EII).

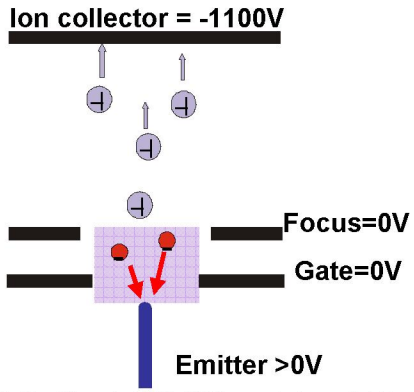

Figure 2: Double-gated VA-CNF operated as a field ionizer.

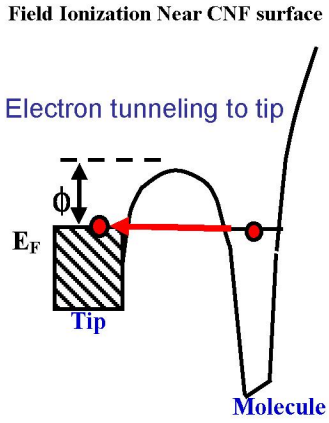

Figure 3: Field ionization: A strong field applied to the tip deforms the energy barrier of molecule allowing electrons to tunnel from the molecule.

technique. The PR was spun on the wafer at a high speed, which PR surface was automatically planarized without using CMP (Fig. 6(c)). This smooth PR layer defined the structure of the gate aperture. Later, an anisotropic silicon reactive ion eth (RIE) was used to remove the a-Si (Fig. 6 (d)). Thus, the gate aperture is then open. After the gate aperture was patterned by RIE, the PR was then removed. Fig 7 shows SEM pictures of an array of a single-gated CNF structure using this technique. (2) Formation of the focus insulator and the focus electrode (step F though J), which could be done by repeating the step A through E. (3) The final step is CNF exposure (step K). The last step of the fabrication process is to remove the oxide between the focus electrode, gate electrode and the CNF field emitter using the buffered oxide etch (BOE). The side view and the top view of a completed double-gated CNF device is shown in Fig 8. This technique offers a very fast, fairly uniform and well-controlled planarization method of making the self-aligned gates, which can replace the CMP technique that has been reported and used by Dvorson et. al, Guillorn et. al, and Chen et. al [6,7,8].

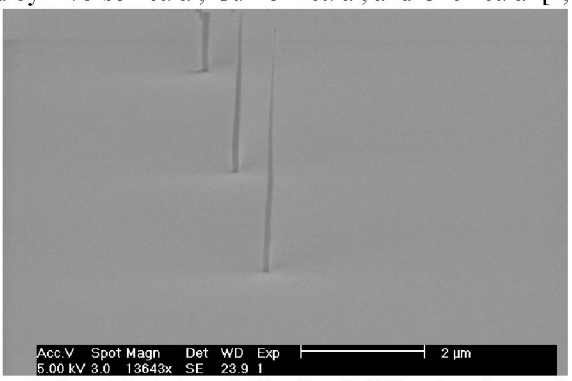

Figure 4: 4 µm-tall single vertically-aligned CNFs using plasma enhanced chemical vapor deposition.

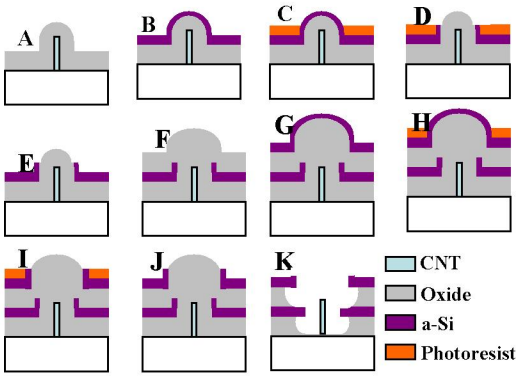

Figure 5: Schematic of the double-gated VA-CNF fabrication process.

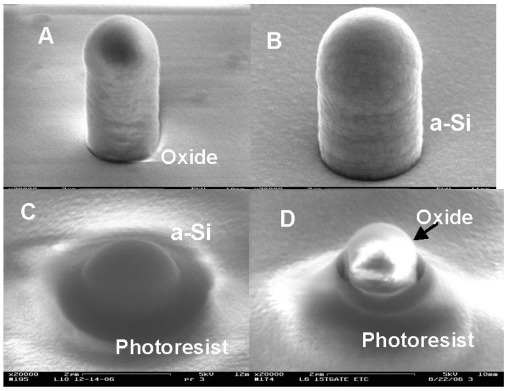

Figure 6: SEMs of (a) a vertically aligned CNF covered by 1.4µm oxide, (b) a 0.4µm conformal layer of doped a-Si on top of the oxide, (c) a layer of PR spun at a high speed, and (d) a-Si was removed to define the gate.

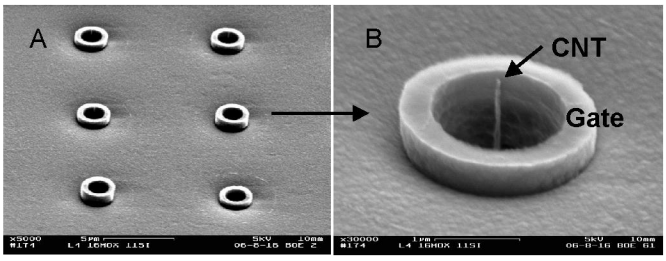

Figure 7: SEM pictures of (a) an array of single-gated CNF FEA and (b) an individual single-gated CNF device.

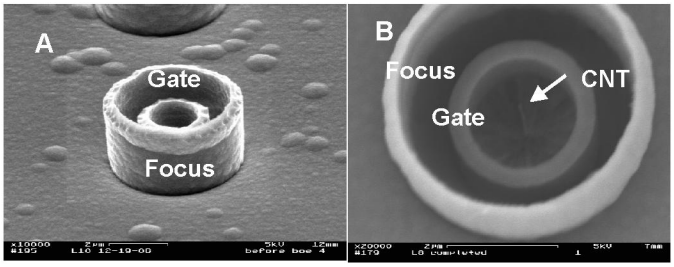

Figure 8: A complete double-gated isolated vertically aligned carbon nanofiber device. (a) The side view and (b) top view of the device.

Ionizer Characterization

The double-gated CNF arrays were first characterized as three-terminal field emitters with the gate and focus biased at the same voltages and a low field emission turn-on voltage of 24V was obtained (Fig. 9 and 10). Next, these arrays were characterized as four-terminal field emitters, in which two gates different biases (Fig. 11). From the Fowler-Nordheim analysis, we obtained focus and gate field factors of 2.71 x 10^5 V/cm and 1.01 x 10^6 V/cm respectively. These values are consistent with values obtained from MATLAB simulations (Table 1). These arrays were used as electron sources for EII at pressures ranging from $5x10^{-6}$ to $1x10^{-3}$ Torr. The ion current is linearly related to the electron current and the ambient pressure (Fig. 12) consistent with the EII model. We obtained a ratio of ion current to electron current of 0.05 which is much higher than typical EII based on thermionic sources. Thus, the device could be used as a gas pressure sensor in vacuum. Another double-gated VA-CNF array was next characterized as a field ionizer. Before characterization as a field ionizer, the field factors were obtained from field emission measurements with the gate and focus tied together. The effective field factor obtained from Fowler-Nordheim analysis is 3.85 x 10^5 V/cm. Argon was allowed to flow into the test chamber through a needle valve until stable pressure was obtained. Our results indicate that the turn-on voltage for field ionization was reduced from 5-10 kV (typical for ungated) to 350 V as indicated in Fig.10. The results also show that the ion current is directly proportional to the ambient pressure (Fig. 13) and exponentially dependent on gate voltage (Fig. 14) as predicted by a barrier model for field ionization presented earlier.

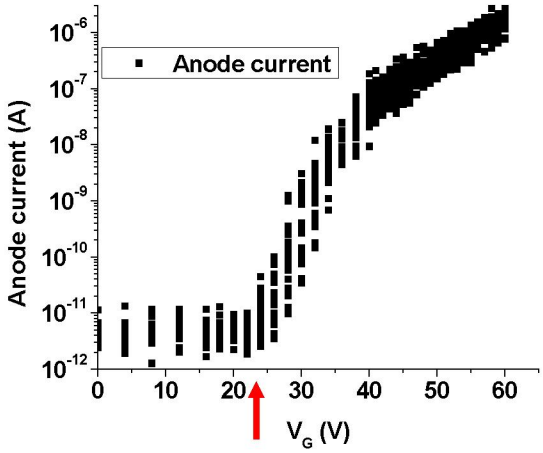

Figure 9: Anode current vs. Gate voltage (V_G) showing repeatable field emission and a turn-on voltage of 24V.

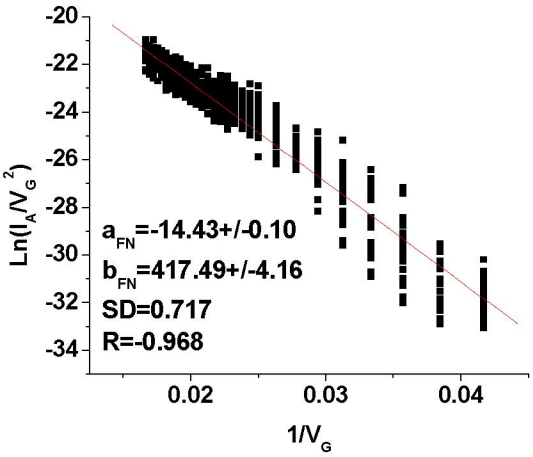

Figure 10: Fowler-Nordheim analysis of the field emission data shown in Figure 9.

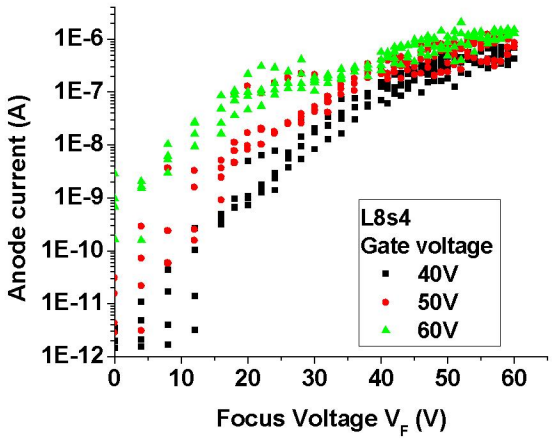

Figure 11: Four-terminal IV data: the focus transfer characteristics of the D-G CNF device (I_A vs. I_F at a fixed V_G).

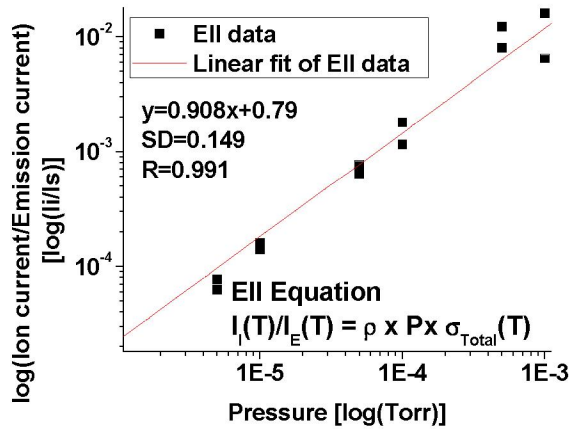

Figure 12: Plot of normalized ion current (I_i/I_S) vs. Pressure showing a linear relationship.

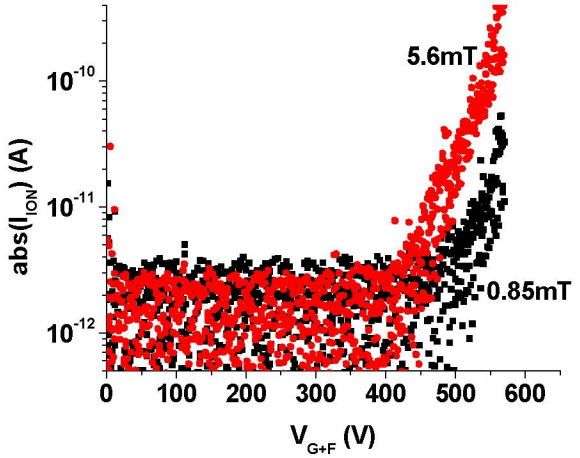

Figure 13: Ion current vs. applied voltage at 0.85mTorr and 5.6mTorr. V_{ION}= -1100V and V_{G+F}=0V.

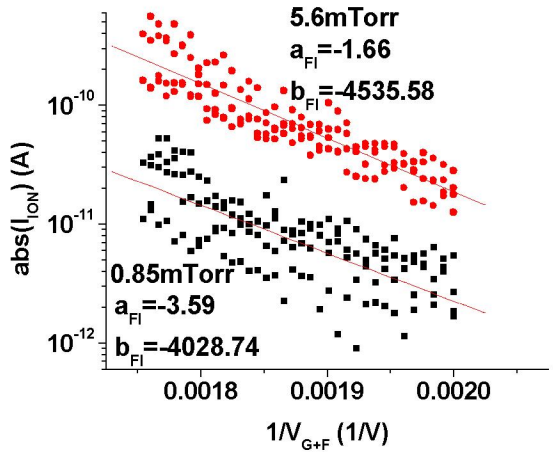

Figure 14. Field ionization analysis of data shown in Figure 10. Plot of Ln(Ii) vs. $1/V_{G+F}$ to extract intercept (a_{FI}) and slope (b_{FI}).

	β_F [V/cm]	β_G [V/cm]	β_F / β_G
4-terminal Data	2.71×10^5	1.01×10^6	0.270
Matlab Simulation	3.07×10^5	1.19×10^6	0.272

Table 1: Summary of IV data and the Matlab simulation of β_F and β_G.

Summary

Double-gated isolated vertically aligned carbon nanofiber arrays were designed and fabricated using a novel photoresist planarization technique. The device successfully ionized the gas molecules in both EII and FI modes of operation. As an EII micro-ionizer, it has a faster response time while using less power than EII based on thermionic emission. As a FI micro-ionizer it has a lower turn-on voltage than conventional ungated field ionizer. This is also the first reported gated FI mode micro-ionizer.

When operated as a field emitted electron impact ionizer, for the same ion current, the ionization efficiency (ratio of ions to emitted electrons) increased from 0.005 to 0.05 and the power dissipation reduced from >1 W to 100 mW. In addition, the second gate protects the VA-CNF from erosion by the ions in EII operation. When operated as a field ionizer, the turn-on voltage for field ionization is significantly reduced from 5-10 kV to 350 V due to the addition of gates that are in close proximity to the VA-CNFs.

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