Microfabricated field emission devices using carbon nanofibers as cathode elements

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The digital electrostatic electron beam array lithography concept under development at the Oak Ridge National Laboratory proposes performing direct write electron beam lithography with a massively parallel array of electron emitters operating simultaneously within a digitally programmable microfabricated field emitter array (FEA). Recently we have concentrated our research efforts on the field emission (FE) properties of deterministically grown vertically aligned carbon nanofibers (VACNFs). We have measured the FE properties of isolated VACNFs using a moveable current probe and found that they have low FE turn-on fields and can achieve stable emission for extended periods of time in moderate vacuum. In order to use the VACNF in microfabricated FEA devices we have subjected them to a variety of processing phenomenon including reactive ion etching and plasma enhanced chemical vapor deposition, and found them to be quite robust. Using these processes we have fabricated operational gated cathode structures with single VACNFs cathodes. The issues involved in this fabrication process and the performance of these devices are discussed. © *2001 American Vacuum Society.* [DOI: 10.1116/1.1420201]

I. INTRODUCTION

Electron beam-based lithography technologies are possible candidates for next generation lithography applications. However, lithography using a single electron beam cannot achieve acceptable wafer throughput levels to become a viable manufacturing technology. The digital electrostatic electron beam array lithography (DEAL) concept under development at the Oak Ridge National Laboratory (ORNL) proposes a massively parallel, maskless and digitally programmable microfabricated field emitter array (FEA) that allows simultaneous writing with many electron beams as a means of circumventing this problem.

An electron beam lithography system based on a microfabricated FEA will require a robust field emission (FE) source with a low turn-on field E_{to} and stable operating characteristics in moderate vacuum. In recent years, the FE properties of nanostructured graphitic carbon-based materials including single-[1–3] and multiwalled[4,5] carbon nanotubes and carbon nanofibers (CNFs)[6,7] have been an area of intense investigation. This body of research indicates that these materials have several advantages over other candidate materials for FE applications, namely very low FE E_{to} and extraordinary environmental stability.[8] Recently, we have focused on vertically aligned CNFs (VACNFs)[6,7] as FE sources for the DEAL application precisely for these reasons. Moreover, VACNFs can be synthesized in a catalytic dc plasma enhanced chemical vapor deposition (PECVD) process,[9] enabling their site-specific synthesis in microfabricated device structures.[10,11] In this article we report on the FE properties of individual VACNFs measured by a moveable probe and the fabrication and operation of integrated gated cathode structures that use a single VACNF as the FE element.

II. FE MEASUREMENTS OF INDIVIDUAL VACNFS

Arrays of VACNFs [Fig. 1(a)] were grown on *n*-type Si substrates using a dc PECVD process.[7,9] These arrays contained conical VACNFs with average base diameters of 200 nm, average tip diameters of 25 nm, and average heights of 2 μm spaced at even intervals of 50 μm. FE properties of individual VACNFs were measured with a moveable current probe capable of positioning a 2-μm-diam probe tip above an individual VACNF with submicron accuracy.[6,7]

FE measurements conducted in a vacuum chamber operating at 5×10^{-7} Torr revealed that isolated VACNFs are good field emitters with emission threshold fields of 15–50 V/μm, and that emission can be spatially uniform over large areas of relatively sparse regions of randomly spaced VACNFs.[6,7] Isolated VACNFs have displayed stable emission for 175 h (the longest period of test) of continuous 10 nA operation at vacuum levels of 10^{-6} Torr. FE current versus voltage $(I-V)$ analysis has shown a maximum measured FE current exceeding 5 μA without any degradation to the VACNF tip. This corresponds to a current density of approxi-

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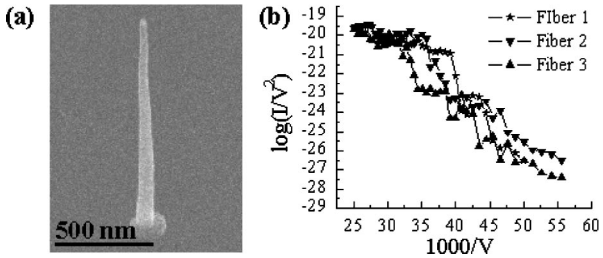

FIG. 1. (a) Scanning electron micrograph (SEM) taken at 45° of an individual VACNF grown from an EBL patterned catalyst site. (b) Fowler–Nordheim plots of scanned-probe FE measurements from three individual fibers. Maximum field emission currents exceeding 5 μA were observed corresponding to a current density of approximately 500 kA/cm^2 for a nominal VACNF tip diameter of 30 nm.

mately 500 kA/cm^2. The FE $I-V$ characteristics of isolated VACNFs typically display Fowler–Nordheim like tunneling behavior. $I-V$ data plotted in Fowler–Nordheim coordinates for three fibers are shown in Fig. 1(b).

III. POST GROWTH PROCESSING OF VACNFS

Recently, we reported a technique for fabricating gated cathode structures that uses a single *in situ* grown VACNF as an FE element.[10] While this technique was capable of realizing these devices, there were some disadvantages to this process. Primarily, the dc plasma discharge used to grow the VACNFs was found to cause charge induced damage to the gating structure. This phenomenon could be controlled by placing an electrostatic potential on the gate during VACNF growth at the cost of introducing complexity into the process. The necessity of biasing the gate during growth decreased the potential of scaling this process to wafer level production, a necessary capability for many applications.

In order to circumvent the limitations inherent to the *in situ* growth process, we examined some alternative routes to building gated cathode structures with VACNF emitters. We ran a series of simple experiments to determine how robust the VACNFs were to processing environments commonly used in microfabrication. We found that isolated unpassivated VACNFs could withstand more than 40 min of reactive ion etching (RIE) in a CHF_3:O_2 rf plasma. VACNFs that were subjected to RIE generally displayed improved FE properties, including a reduction in the FE E_{to}. This is presumed to be a consequence of increased nanometer- and subnanometer-scale roughness of the VACNF tip by the RIE process. We also observed that it was possible to coat patterned arrays of VACNFs in conformal layers of SiO_2 deposited by silane-based rf PECVD processes [Figs. 2(a) and 2(b)]. We found that it was possible to remove this oxide layer using CHF_3-based RIE processes without damaging the VACNFs [Figs. 2(c) and 2(d)]. Based on these results we were able to design a fabrication process that was more amenable to wafer scale production than the one previously reported.[10]

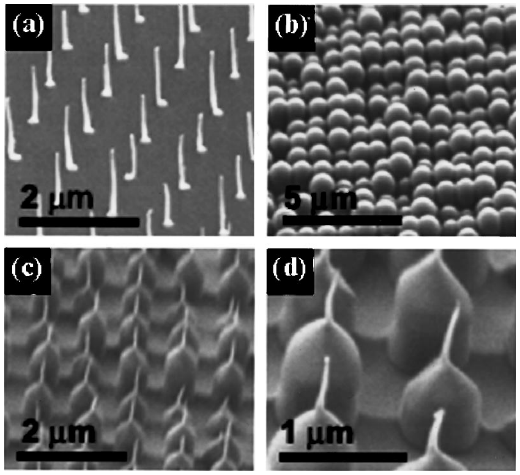

FIG. 2. Deposition and removal of conformal PECVD SiO_2 on VACNF arrays. (a) VACNF array on Si as grown (b) following the deposition of a 1-μm-thick PECVD SiO_2 layer (c),(d) after 40 min of RIE using a CHF_3/O_2 plasma. All micrographs were taken in a SEM at a 45° angle.

IV. VACNF GATED CATHODE FABRICATION

A diagram of the gated cathode fabrication process is shown in Fig. 3. 3 in. low resistivity *n*-type Si wafers were used as substrates throughout this work. Prior to performing any processing, the substrates were cleaned in a solution of ammonium fluoride and hydrofluoric acid 6:1 for 60 s to remove any native oxide from the substrate surface. Immediately following this cleaning the substrates were spin coated with a bilayer of poly(methylmethacrylate) as described in Ref. 10.

High-resolution direct write electron beam lithography (EBL) was used to define the first layer of features consisting of the VACNF catalyst sites, and global and die-level registration marks for subsequent photolithography steps. A Leica VB6-HR with a 100 keV thermal field emission source was used to perform the EBL exposures. A beam current of 1 nA and a pixel size of 5 nm were used to pattern all of the features on this layer. An electron area dose of 1000 μC/cm^2 was used to expose the VACNF catalyst sites. The sites were patterned as 40 nm octagons on a 50 μm pitch in a 3×3 array and were intentionally overexposed to produce 50 nm circular dots. All other features on this layer were exposed with a dose of 800 μC/cm^2. A 5×5 array of die was patterned onto each substrate with 10 mm spacing between die.

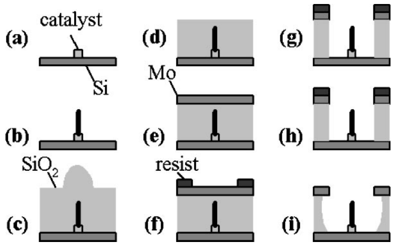

FIG. 3. Process flow for the fabrication of the VACNF-based gated cathode structures.

The electron beam exposures were developed in a solution of methylisobutylketone:isopropanol 1:3 for 1 min with no agitation.

Using an electron gun physical vapor deposition (PVD) system, the substrates were metallized with a bilayer consisting of 100 Å of Ti and 100 Å of NiFe alloy (1:1). Pattern transfer was performed using a liftoff technique. VACNFs were grown onto the wafers using a process similar to the one reported earlier[9,10] [Fig. 3(b)]. The principle difference in the present work is that the growth was conducted on whole 3 in. wafers. The VACNFs produced for this work were conical in shape with an average base diameter of 200 nm, average height of 1 μm, and average tip radius of curvature of 20 nm.

A 2.5-μm-thick conformal layer of SiO_2 was deposited onto the substrates by a silane-based rf PECVD process operated at a chamber temperature of 275 °C [Fig. 3(c)]. Chemical mechanical polishing (CMP) (Strasbaugh 6EC) was used to planarize the structures [Fig. 3(d)]. The SiO_2 layer was polished until all gross surface nonuniformities had been removed, producing a final oxide thickness of approximately 1.5 μm. Photoresist was applied to the substrates and the gate electrode pattern was exposed [Fig. 3(e)]. This pattern consisted of a 3×3 array of 10 μm square electrodes individually contacted by macroscopic probing pads and aligned to the 3×3 array of VACNF emitters buried beneath the SiO_2 layer. Following the exposures the substrates were developed in a standard aqueous photoresist developer. A 10-nm-thick layer of Ti followed by a 40-nm-thick layer of Mo was deposited onto the substrates using electron gun PVD [Fig. 3(f)]. Pattern transfer in this step was performed by a liftoff technique.

A final photolithography step was performed at this time to define an aperture in the extracting electrode. Resist was applied to the substrates and an auto-aligning I-line stepper (GCA AS200) was used to perform the exposures. This tool is capable of achieving overlay of less than 50 nm with respect to preexisting EBL defined features, demonstrated in our previous work.[10] The exposed pattern in the present work consisted of 2 μm apertures aligned concentrically with the buried VACNF emitter. Using the resist as an etch mask the substrates were subjected to A CF_4/O_2 RIE to pattern the Mo/Ti gate layer followed by a CHF_3/O_2 SiO_2 etch [Fig. 3(g)] to release the buried VACNF. The structures were dipped into a dilute HF solution (10:1, de-ionized water:HF) for 1 min to create undercut in the well sidewall profile [Fig. 3(h)] to prevent charging of the well sidewalls during device operation. Finally, the photoresist was removed in acetone [Fig. 3(i)], completing the structure. A micrograph of a finished device is shown in Fig. 4.

V. OPERATION OF VACNF GATED CATHODES

Operational tests of the gated cathode structures were performed in a chamber evacuated to a pressure of 10^{-6} Torr producing a test environment similar to the expected and less than ideal operating environment. A flat Cu anode was placed 700 μm directly above the Si substrate containing the VACNF-based FE device. A Hewlett Packard 4156A Precision Semiconductor Parameter Analyzer containing four dc source measure units (SMU) was connected to the cathode, gate, and anode. All of the data presented in this work were obtained with the gate at ground potential, and a 100 V positive bias on the anode. Anode and gate currents were measured as the cathode potential was varied between ground and −100 V.

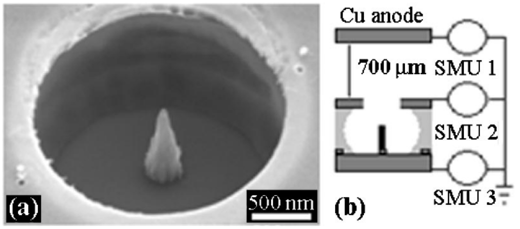

FIG. 4. (a) SEM of a completed gated cathode structure taken at a 35° angle. (b) Diagram of the FE measurement setup for the gated cathode testing.

Initial FE $I-V$ curves revealed typical FE E_{to} of 75 V/μm, corresponding to a gate-to-cathode bias voltage V_{gc} of 85 V. The structures were not cleaned in any way prior to operation, ensuring the presence of an adsorbate layer on the VACNF. To remove contamination from the tips, constant bias measurements of the emission current were conducted setting V_{gc}=90 V for 10 min continuously. A plot of the initial 60 s of the device operation in this mode is shown in Fig. 5(a). It is clear from these data that there is a marked increase in the FE current measured by the anode after 40 s, averaging 700 nA over the full duration of the test. However,

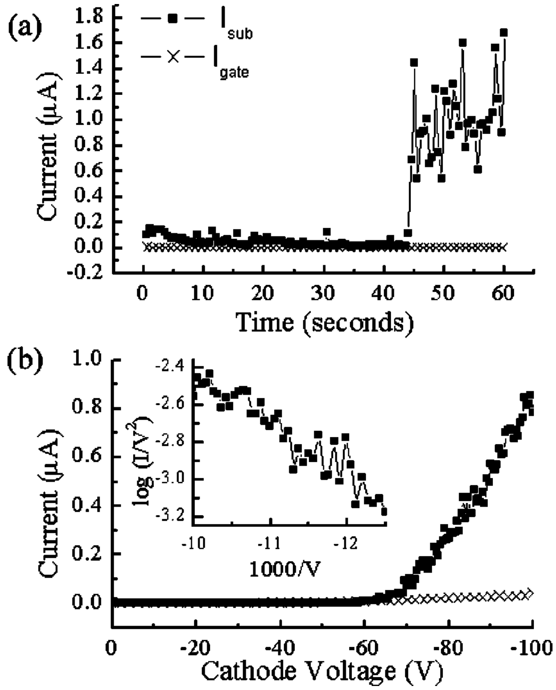

FIG. 5. Operating characteristics of a VACNF-based gated cathode. (a) Constant bias operation using V_{gc}=90 V. (b) FE $I-V$ curve taken with a 22 MΩ ballast resistor in series with the cathode and SMU following 20 min of constant bias operation. (Inset) Fowler–Nordheim plot of these data.

there was no apparent increase in the gate current, which averaged less than 2 nA over the entire test. This corresponds to less than 1% of the average emitted current being collected by the gate electrode, indicating that the emission is well collimated. An FE $I-V$ curve with a 22 MΩ ballast resistor in series between the cathode and the SMU is shown in Fig. 5(b). The ballast resistor was added as a feedback mechanism to suppress noise. These data were taken after 20 min of constant bias testing and show a reduction in FE E_{to} to approximately 60 V/μm, corresponding to a V_{gc} of 65 V. This observation is most likely attributed to emitter conditioning during constant bias FE operation.

VI. CONCLUSIONS

We have investigated the FE properties of isolated, deterministically grown VACNFs using a scanning current probe. VACNFs have excellent FE properties and are among the most promising materials for FE applications. Processing experiments were conducted with the VACNFs and show that they can survive CHF_3-based RIE and PECVD SiO_2 deposition and removal. This allowed us to develop a wafer scale production process for VACNF-based FEAs that uses standard microfabrication techniques and offers several possibilities for variation. For example, an adaptation of the process demonstrated by Lee *et al.*[12] for producing FEAs by CMP with gate apertures self aligned to the emitter tip could be used to produce similar self-aligned VACNF-based FEAs.

The operation of a gated field emitter using a single VACNF as the FE cathode was also demonstrated. This device is capable of operation in moderate vacuum and can achieve high operating currents for extended periods of time. Although the FE E_{to} may appear somewhat high for these devices compared to isolated VACNFs, it is in reasonable agreement with the values expected from the VACNF aspect ratio[7] and the geometry of the well. By decreasing the diameter of the gate aperture and increasing the aspect ratio of the VACNF, it should be possible to lower the operating voltage of these devices significantly. The low percentage of the emitted current measured at the gate electrode indicates that the emitted electron beam is well focused and demonstrates that VACNF-based FE devices are ideal for cold cathode FE applications such as the DEAL massively parallel EBL system being developed at ORNL.

ACKNOWLEDGMENTS

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