Forms and behaviour of vacuum emission electronic devices comprising diamond or other carbon cold cathode emitters

BY J. L. DAVIDSON*, W. P. KANG, K. SUBRAMANIAN AND Y. M. WONG

Department of Electrical Engineering and Computer Science,
Vanderbilt University, Nashville, TN 37235, USA

Nanocarbon-derived electron emission devices, specifically nanodiamond lateral field emission (FE) diodes and gated carbon nanotube (CNT) triodes, are new configurations for robust nanoelectronic devices. These novel micro/nanostructures provide an alternative and efficient means of accomplishing electronics that are impervious to temperature and radiation. For example, nitrogen-incorporated nanocrystalline diamond has been lithographically micropatterned to use the material as an electron field emitter. Arrays of laterally arranged ‘finger-like’ nanodiamond emitters constitute the cathode in a versatile diode configuration with a small interelectrode separation. A low diode turn-on voltage of 7 V and a high emission current of 90 μA at an anode voltage of 70 V (electric field of approx. 7 V μm⁻¹) are reported for the nanodiamond lateral device. Also, a FE triode amplifier based on aligned CNTs with a low turn-on voltage and a small gate leakage current has been developed.

Keywords: nanodiamond; carbon nanotube; field emission; vacuum diode and triode

1. Introduction

Field emitter arrays need improved novel cold cathode materials for better and more reliable performance. The presence of negative electron affinity on hydrogen-terminated diamond surfaces, coupled with the practical chemical vapour deposition (CVD) processing of deposited diamond as a thin film on a variety of substrates, has promoted further interest in the use of diamond and diamond-like carbon materials as field emitters (Zhu 2001). Experimentally, diamond and carbon nanotube (CNT) emitters have been observed to emit electrons at relatively low electric fields and generate useful current densities. In this work, nanocarbon-derived vacuum devices, namely the nanodiamond lateral diode and the gated CNT triode, are examined. The material properties, device structure and fabrication process, and the electrical performance of the two configurations are presented.

* Author for correspondence (jim.davidson@vanderbilt.edu).

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2. The nanodiamond lateral field emission device

(a) Introduction

Nitrogen-incorporated nanodiamond has proved to be an efficient electron-emitting material (Zhou et al. 1997; Wu et al. 1999; Wang et al. 2003; Subramanian et al. 2006a). The characteristic properties of the nanodiamond film including smaller grain size (5–10 nm; Subramanian et al. 2005a), smoother surface morphology, increased sp²-carbon content and higher electrical conductivity (Subramanian et al. 2006a,b) favour electron field emission (FE). The use of the material for device applications in vacuum microelectronics calls for the development of well-defined nanodiamond emitter microstructures, as FE from uniformly sharp microtips of diamond exhibits significant enhancement in the total emission current and stability over time. As diamond micropatterning process techniques have developed, more sophisticated FE cathodes and devices are possible. The nanodiamond lateral FE device represents a new category of diamond-based electronics, made possible from the development of a consistent micropatterning process capable of achieving desirable micro/nanostructures from the material. The lateral device, in a diode configuration, has uniform arrays of nanodiamond fingered emitters with a high aspect-ratio geometry forming the cathode, in close proximity with the anode structure, with equal interelectrode spacing distribution over a large area. The nanodiamond lateral finger array FE diodes have a low voltage and a potential for a high emission current operation (Subramanian et al. 2005b).

The processing of field emitters or their exposure to ambient conditions may result in contaminated surfaces (Schwoebel & Brodie 1995). It has been observed that electron emission is highly dependent on the cleanliness of the emitter surface. The current–voltage (I–V) characteristics of microfabricated field emitters are governed by the surface structure and chemical composition of the emitters, which define the electron-tunnelling barrier at the surface (Schwoebel et al. 2003). Adsorption of common contaminants can increase the work function at the emission sites, which affects the emission current, the device-operating voltage, as well as the current stability over time. Also, the non-uniform emission current generation between tips in a large emitter array decreases the average current per tip, thereby dropping the current density of the device. Hence, it is important to develop efficient tip-conditioning techniques to improve emission performance. The results of effective post-fabrication tip-processing procedures conducted on the nanodiamond lateral FE devices are reported here.

(b) Experimental

The lateral device processing approach has been reported in detail in previous publications (Subramanian et al. 2005b, 2006c). A nitrogen-incorporated nanodiamond film grown by CH₄/H₂/N₂ microwave plasma-enhanced CVD on a silicon-on-insulator (SOI) wafer is micropatterned using a pure oxygen plasma chemistry reactive ion etch (RIE) in an inductively coupled plasma–RIE system. The lateral device patterns are lithographically defined on an aluminium mask and transferred onto the nanodiamond layer by RIE with high selectivity at an etch rate of approximately 0.5 μm min⁻¹. On etching the active silicon layer of the SOI wafer, the isolation of the nanodiamond lateral electrodes is achieved by

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means of the underlying 4 μm thick SiO₂ layer. The properties of the nanodiamond film have been examined and quantified (Subramanian et al. 2005a, 2006a,b). The scanning electron microscopy (SEM) of a microfabricated nanodiamond lateral FE diode is shown in figure 1.

A 125-finger array nanodiamond lateral diode was used for the emitter tip-processing experiment. The device, as fabricated, was characterized for FE in a vacuum level of 10⁻⁷ Torr and the FE I–V behaviour recorded. To examine the effect of emitter surface cleaning treatments on the lateral diode performance, the nanodiamond device was subjected to wet chemical processing as well as in situ vacuum tip-conditioning methods. The silicon wafer industry’s standard process technology RCA chemical cleaning procedure was applied to remove the contaminants present on the surface of the nanodiamond accumulated at the terminus of the lateral device processing. The device was immediately transferred to the vacuum FE test chamber where in situ techniques were executed for more localized cleaning of the nanodiamond emission sites by contaminant thermal desorption. A vacuum–thermal–electric (VTE) treatment was applied to the lateral device, where the nanodiamond fingered emitter arrays were simultaneously ‘soaked’ at a low emission current under moderate heat and applied electric field and a vacuum of 10⁻⁷ Torr. The device was maintained at 150°C for several hours while the emission current was kept below 2 μA by adjusting the anode voltage. The VTE treatment was terminated when a stable current was obtained for a period of time of approximately 1 hour. The device was then cooled down slowly to room temperature. Lastly, without the application of an external heat source, the nanodiamond lateral emitters were maintained at an emission current of 20 μA for approximately 1 hour during normal vacuum diode operation, where the extracted FE current was used to further clean the finger tip locally by controlled self-heating. After this tip conditioning, the I–V characteristics of the 125-fingered nanodiamond lateral diode were again obtained.

(c) Results and discussion

Figure 2 portrays the effect of nanodiamond emitter tip conditioning on the FE characteristics of the 125-fingered lateral device. As fabricated, the lateral diode exhibited a turn-on voltage of approximately 25 V and
approximately 6 μA emission current at an anode voltage of 95 V. The emission current value determining the turn-on voltage of the diode was 100 nA. Upon tip conditioning, significant emission enhancement was observed from the nanodiamond lateral emitter array, resulting in the demonstration of a very low diode turn-on voltage of 7 V and a high emission current of 90 μA at an anode voltage of approximately 70 V. The enhancement in the $I$–$V$ behaviour was accompanied by the reduction in the slope of the Fowler–Nordheim (F–N) behaviour (figure 2, inset), which clearly indicates a decrease in the work function of the emitter tip material and/or increase in the field enhancement factor by tip conditioning. This emission characteristic was found to be repeatable and irreversible after tip processing. All data shown in figure 2 were captured at room temperature in a vacuum environment of $10^{-7}$ Torr. The negative linear slope of the F–N plots confirms that the FE characteristics of the nanodiamond diode follow the Fowler–Nordheim behaviour. Figure 3 portrays the effect of the experiment on the emission stability obtained from the lateral device. A fluctuation of less than 4% was observed about an emission current of 5 μA over an 80 min time period with no monotonic current decrease with time at a constant applied voltage.

Effective tip-processing techniques have been shown to improve the electron emission performance of several materials including CVD diamond microtip arrays (Kang et al. 1998). Appreciable cleaning of the surface of emitters, especially by thermal desorption of contaminants, can decrease and restore the work function ($\Phi$) of the emitter material. Another hypothesis proposes that surface treatment results in tip deformation due to the field-forming process. The field-forming process has been shown to provide FE enhancement for
metal (molybdenum) cathode tips (Spindt et al. 1991). According to the field-forming process, the tip is reformed into a configuration that increases the electric field locally on the tip surface for a given applied field, thereby increasing the field enhancement factor ($\beta$). Both $\beta$ and $\Phi$ are critical factors for electron FE. It should be noted that post-fabrication conditioning/processing techniques are also common in the conventional silicon integrated circuits fabrication technology, such as the rapid thermal annealing treatment performed following an ion implantation step to repair the primary crystalline damage in the silicon. We have seen no evidence of field forming in nanodiamond emitters.

The lateral diamond emitter devices have also undergone preliminary evaluation for their behaviour at extended operational levels such as temperature and radiation. Figure 4 illustrates the emission as a function of temperature; note the total independence of the device forward current on temperature. Also, such a device was subjected to up to 15 Mrad of radiation flux with no effect on its performance (figure 5). Furthermore, example devices have been assembled in vacuum cavity packages (figure 6) and operate in a 'conventional electronic' configuration. Test devices have passed more than 1000 hours of operation in these packages and remain functional and unchanged. Finally, a triode configuration (figure 7) is under evaluation. This device, which has transistor-type properties, is the subject of another paper.

**(d) Summary**

Nanodiamond lateral FE devices can be suited for a high-speed and high-power performance. Emitter tip conditioning has been shown to help promote emission stability, improve emission uniformity for more reliable array operation, high current performance and low-voltage device operation.

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3. CNT vacuum triode

(a) Introduction

Solid-state power amplifiers are the dominant device in the field of very high-frequency and high-bandwidth microelectronic applications. However, their maximum output power is limited to a couple of watts at 30 GHz (K-band; Milne et al. 2004). Consequently, most of the high-frequency power amplifiers in use
today for applications in radar, long-range telecommunications and space applications are travelling wave tube (TWT) amplifiers based on thermionic emission (TE). An X-band miniaturized TWT amplifier based on ‘Spindt-type’ FE arrays has been demonstrated at 11.5 GHz with a saturation output power of 28 W and a saturation power gain of 40 dB (Makishima et al. 1999). High-frequency FE-based amplifiers possess many attractive features such as less bulky, instant-on and operating at a lower voltage than a TE-based amplifier.

Recently, our group has demonstrated an FE triode amplifier based on aligned CNTs synthesized by a microwave plasma-assisted chemical vapour deposition (MPCVD) method (Wong et al. 2005). The gated FE device with convex-shaped CNT emitters has demonstrated favourable triode amplifier behaviour with low gate leakage current, a large DC gain of approximately 352, a low gate turn-on voltage of approximately 25 V and useful AC gain. The convex-shaped emitters have variable CNT heights with shorter tubes on the circumferential region. According to simulations on a nanotriode using SIMION 3D v. 7.0 software
(Scientific Instrument Services, Inc.; Nicolaescu et al. 2003, 2004), it was found that gated CNT emitters with variable height displayed more quasi-uniform electric fields on the CNT tips than the one with uniform height, and less chance of CNTs burning out due to overactive emitters located on the circumferential region nearest to the gate electrode. CNTs possess the advantages of very high aspect ratio, small radius of curvature, lack of vacuum-arcing, chemical inertness and thermal stability compared with other field emitters. In this study, we report the development of a CNT FE triode amplifier with low turn-on voltage and small gate leakage current using a dual-mask microfabrication process.

(b) Device fabrication and characterization

The dual-mask fabrication process of the CNT triode began with the thermal oxidation of a highly doped Si substrate, as depicted schematically in figure 8. Molybdenum (Mo) was then sputter-deposited using a DC magnetron sputtering system as the gate electrode. The thicknesses of the gate electrode and the thermal oxide (SiO$_2$) were approximately 0.3 \( \mu \)m and approximately 1.5 \( \mu \)m, respectively.

Figure 8. Fabrication process of the CNT triode depicted schematically. (a) Sputter deposition of Mo on oxidized Si substrate, (b) first mask: gate patterning and etching of Mo, (c) second mask: cathode patterning, etching of Mo and SiO$_2$ and (d) catalyst deposition, photoresist lift-off and CNT synthesis.
Next, conventional photolithography was performed with the first mask to define and pattern the gate electrode area. This gate-patterning step serves an important purpose of minimizing the cathode–gate capacitance for a potential high-frequency operation. Subsequently, the Mo was wet-etched by a commercial aluminium etchant (power-added efficiency, PAE), an acid mixture of H₃PO₄, HNO₃, HAc and H₂O. Next, a second mask was used to align and pattern an array of 2 µm × 20 µm rectangular microcathodes within the defined gate area. A second wet-etching of Mo was then performed followed by the wet-etching of the SiO₂ underneath the gate by a buffer oxide etch. A bi-metal layer of titanium (Ti), acting as a diffusion barrier layer, and nickel (Ni), the CNT growth catalyst, was then sputter-deposited in sequence on the vacuum FE triode sample by DC magnetron sputtering without breaking the vacuum. The surplus catalyst on the gate electrode was then removed by a photoresist lift-off technique in acetone followed by the selective growth of convex-shaped aligned CNTs by MPCVD technique, as described in detail elsewhere (Wong et al. 2005).

The FE measurements were performed at room temperature in a vacuum chamber evacuated to a base pressure of 10⁻⁶ Torr, a relatively realistic and achievable vacuum level should the device be vacuum-sealed later in package form. The CNT triode was tested in a common-emitter configuration and a computerized data acquisition system equipped with LABVIEW program (National Instruments) was employed for the measurements of the anode emission current (Iₐ) and the gate current (Iₔ) as a function of the gate voltages (Vₔ) at a constant anode voltage (Vₐ) of 1000 V.

(c) Results and discussion

In contrast to the TE-based triode, the high-frequency operation of a FE triode is dictated by the cut-off frequency (fₜ) and not the electron transit time (Neidert et al. 1991). fₜ is dependent on the ratio of transconductance (gₘ) to the overlapping interelectrode capacitance (Cₔ), and can be expressed as

\[
fₜ = \frac{gₘ}{2\pi Cₔ}.
\]

Accordingly, in order to improve the high-frequency performance of the CNT triode amplifier in this study, Cₔ was reduced by performing a dual-mask photolithography process to minimize the gate area, as shown in figure 9. In addition, a thick cathode–gate insulating layer of approximately 1.5 µm was adopted to further minimize Cₔ.

The SEM in figure 9a shows part of the 2 × 20 µm rectangular CNT triode array with 1280 array cells. Uniform gate patterning and selective growth of CNTs were observed. High-magnification SEM of the convex-shaped CNT emitters with a decreasing height towards the circumferential region is shown in figure 9b. In this study, the rectangular-shaped CNT emitter arrays have the advantage of larger emission site and hence potentially higher gₘ in return. However, an elongated gate aperture design results in lower array packing density and higher applied voltage to obtain the same field as circular arrays (Spindt et al. 1991).

A plot of the anode current, Iₐ, and the gate current, Iₔ, versus the applied gate voltage, Vₔ, at a constant anode voltage of the gated CNT field emitters is shown in figure 10. The CNT triode displayed a gate turn-on voltage of
approximately 44 V for a measured $I_a$ of 1.0 nA and $V_a$ of 1000 V. The triode array achieved a high current density of approximately 1.9 mA cm$^{-2}$, averaged over the cathode area, at $V_g \approx 69$ V and $V_a \approx 1000$ V. Moreover, a low gate leakage current or $I_g/I_a$ ratio of less than 3% was achieved, critical in the ultimate attainable power gain and long lifetime operation of the triode amplifier. The low gate currents observed demonstrate that the convex-shaped gated CNT emitter is indeed an optimum triode structure as per simulations (Nicolaescu et al. 2003, 2004) and effective in alleviating cathode–gate leakage problems commonly encountered by other triode-type field emitters (Chen et al. 2001; Huh et al. 2003; Jang et al. 2003; Yu et al. 2004).

Neglecting the effect of the applied $V_a$ on the CNT triode, an F–N plot of $\ln(I_a/V_a^2)$ versus $1/V_g$ of the corresponding emission data is shown as an inset in figure 10. The linearity of the F–N plot suggests that the FE or electron-tunnelling behaviour is observed and the electron emission of the triode is mainly induced or extracted by $V_g$ and the anode acting exclusively as an electron

Figure 9. (a, b) Dual-mask photolithography process with a rectangular CNT triode array of 1280 array cells.
Hence, a positive amplification factor can be expected of the triode amplifier. In addition, the negative linear slope of the F–N curve confirms that the FE characteristics of the CNT triode arise from the F–N behaviour.

(d) Summary and conclusions

A CNT triode amplifier using a dual-mask photolithography patterning technique was fabricated and characterized. The CNT triode has a minimum active gate area and a thick SiO2 insulator suitable for a potential high-frequency operation. The FE results show that the improved CNT triode has a gate turn-on voltage of approximately 44 V, and low gate currents of less than approximately 3% of the anode currents. The observed low gate leakage currents confirmed the effectiveness of the convex-shaped gated CNT emitter in alleviating the cathode–gate leakage problem commonly plaguing the operation of a FE triode.

Computing, sensing, amplifying, switching and other critical electronic functions are presently conducted through the manipulation of charge in a solid semiconductor, to and fro through junctions. This incurs performance-limiting heat, capacitance, breakdown as well as significant expense. In fact, the limiting technology for advancing electronics is solid-state semiconductors, whether a silicon or new ‘beyond silicon’ (e.g. silicon carbide, gallium nitride) material. An approach that bypasses this 50 year old transistor technology manages electron flow in a vacuum, not unlike the original vacuum tube, but nanosized down. As described in this paper, electrons are emitted from a highly efficient diamond or CNT tip array, which can be turned on with almost no losses and turned off with unexcelled stand-off. This work has demonstrated the

Figure 10. Anode current, $I_a$, gate current, $I_g$, versus the applied gate voltage, $V_g$, at a constant anode voltage of the gated CNT field emitters shown in figure 9.
diode- and gate-controlled behaviour and is being developed for greater power density and deployable packaging. The diamond emission devices will not require the level of power, cooling and protection infrastructure presently necessary for solid-state electronics, ushering in an era of ‘new electronics’.

References


