Gated Carbon Nanotube Field Emission Enhancement and Regeneration by Hydrogen

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ABSTRACT

We report large increases in field emission current when operating carbon nanotubes in substantial pressures of hydrogen, especially when the nanotubes were contaminated. We have previously demonstrated two different configurations of integrally gated carbon nanotube field emitter arrays (cNTFEAs), CNTs grown inside microfabricated gate apertures with and without silicon posts [1-4]. Salient features of these in-situ grown microgated cNTFEAs include the absence of electrical arcing, low operating voltage, and enhancing effect of some residual ambient gases. Operating both configurations of cNTFEAs without special pre-cleaning in greater than 10^{-5} Torr hydrogen produced orders of magnitude enhancement in emission. For a cNTFEA intentionally degraded by oxygen, the operation in hydrogen resulted in a 340-fold recovery in emission. The results suggested a dependence on atomic hydrogen produced from the interaction between emission electrons and molecular hydrogen. The observed emission enhancement could be due to removal of oxygen-containing surface species, a surface dipole formation, or hydrogen doping.

Keywords: carbon nanotubes, field emission, field emitter arrays, gate apertures, hydrogen

1 INTRODUCTION

Carbon nanotubes have become premier candidates for use as field emitters because of their large geometric field enhancement/low voltage operation, lack of electrical arcing (due to the lack of a surface oxide [5]), and robustness with certain ambient gases (due to the relative chemical inertness and high work function of carbon). These combined qualities overcome many of the shortcomings of conventional metal and silicon tip FEAs. Potential applications include flat panel displays, high frequency amplifiers, spacecraft electric propulsion systems, high voltage and high temperature electronics, miniature mass spectrometers and x-ray sources, multi-beam electron beam lithography, etc.

Most of the published nanotube field emission work involved a diode configuration in which the cNTs, either grown or placed as dense mats on substrates, were placed at a known separation (usually many tens of microns) from an anode. Although the nanotubes produce emission at very low electric fields, the operating voltages are too high for most applications (usually hundreds of volts). In order to reduce the gate voltage, we have grown multi-walled cNTs inside microfabricated gates. We have demonstrated two different configurations of gated cNT field emitters; one consists of cNTs grown on top of gated silicon posts [1] and the second cNTs grown inside open gated apertures [2]. Five patents have been awarded to the Navy on these cNTFEAs [3]. Turn on-voltages below 20 volts and current densities up to 1mA at 40 volts from a 33,000-cell array with 0.5 mm^2 area were measured [1,4]. In addition, we observed a high degree of robustness such as a lack of arcing, emission unaffected by xenon and high temperature, and enhancements by water vapor and hydrogen [4]. We previously observed a 60% increase in emission in 1.5 x 10^{-5} Torr hydrogen, in which case the cNTFEA had been carefully degassed and cleaned [4]. In the same experiment, about a 20% emission enhancement was observed at 1 x 10^{-6} Torr hydrogen. This is to be contrasted with the lack of any effect observed by Dean et. al. [6] at 1 x 10^{-6} Torr H_2 from their ungated single walled carbon nanotube emitter. Wadhawan et. al. [7] observed no effect due to 1 x 10^{-7} Torr hydrogen on their ungated nanotubes.

Studies by Dean et. al. [6] and Wadhawan et. al. [7] have shown that nanotube emission can be adversely and sensitively affected by oxygen contamination. Since the surface of as-grown nanotubes can be in various stages of contamination, including oxygen-containing groups, our motivation is to "clean up" the nanotube surface by operating the emitters in hydrogen. One expects the emission enhancement to depend on the degree of initial contamination. Our present investigation demonstrates that operation in hydrogen can indeed recover emission from even severely contaminated cNTFEAs, resulting in very large enhancement factors. These findings have implications in regard to emitter lifetime and cost-savings.

2 EXPERIMENTAL

CNTFEAs in both the cNT-on-Si post and the cNT-in-open aperture configurations were used in the present investigation. With the exception of some modifications to the former, the details of the fabrication were the same as those published in Refs. [1] and [2], respectively, for the 2 designs.

2.1 Modified Fabrication of cNT-on-Si Post

The structure and fabrication of the gated device were slightly different from those described in our earlier

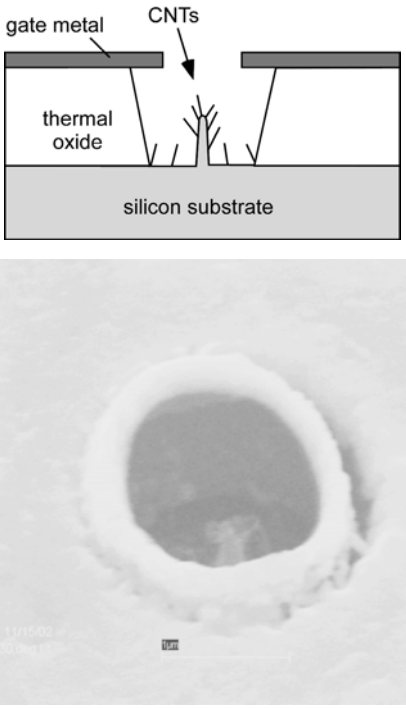

Fig.1. Gated carbon nanotube-on-silicon post field emitter cell at 30° tilt angle. Top: schematic drawing of cell; bottom: SEM of cell with nanotubes on a silicon post centered in a 2.5 micron diameter Pt gate aperture.

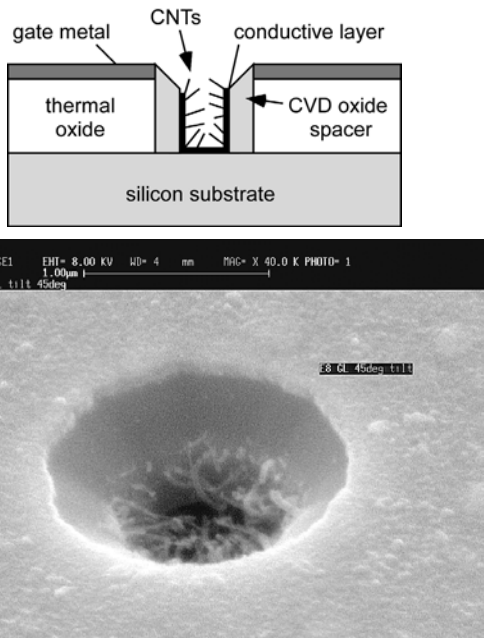

Fig.2. Gated carbon nanotube-in-open aperture emitter cell at 45° tilt angle. Top: schematic drawing of cell; bottom: SEM of cell with nanotubes grown on the sidewall oxide spacer (and cell bottom). The gate diameter and the oxide spacer thickness are 1.7 and 0.35 microns, respectively.

publication [1]. Isotropic etching reduced the height and the diameter of the silicon post to about 1 micron and 0.25 micron, respectively. The gate material was platinum instead of chromium. A thin layer of Ti was sputter deposited before sputter-deposition of the Ni catalyst (~200A). Instead of a HF dip to lift off catalyst from the oxide regions, glancing-angle sputtering at 15° from the substrate was used to remove the catalyst from the top surfaces of the substrate. All other growth parameters were the same as previously [1] (same hot-filament assisted cold wall CVD reactor, same temperatures and gas (ethylene and ammonia) flow rates). The resulting cell structure consisted of multi-walled nanotubes protruding from the top of the Si post in a generally random direction and is shown in the scanning electron micrograph in Fig. 1. Only a very small fraction of the cells contained nanotubes on the Si posts in this array of 3840 cells.

2.2 Fabrication of cNT-in-Open Aperture

The cNTFEA with the open aperture design was from the same sample as the one published in Ref. [2]. Open apertures were first reactive-ion-etched through chrome/silicon gates and silicon dioxide insulator on a silicon substrate. A sidewall silicon dioxide spacer was formed by conformal silicon dioxide layer deposition by CVD, followed by etch back. Fe catalyst was sputter-deposited onto the sample consisting a small arrays of 10 to 40 cells, followed by 15° glancing angle sputter-removal of the Fe from the top surface. Hot-filament assisted CVD described in Ref. [2] was used to grow the nanotubes inside the apertures, including on the vertical sidewall spacer. Figure 2 shows a scanning electron micrograph of such a cell.

2.3 Emission Measurements

Current-voltage emission characterization for both configurations of emitters was carried out in an UHV chamber (base pressure 10^{-10} Torr) equipped with a load lock, sample stage heater, and computerized data collection. Tungsten probes contacted the cathode (substrate) and the gate and the emission was collected on an anode probe biased at 200 V and placed about 1 mm from the sample. Hydrogen was admitted through a leak valve and dynamically pumped using an oil-free turbo-molecular pump. For anode current-time measurements (Fig. 5), a separate turbo-pumped chamber (base pressure 10^{-8} Torr) was used. The gate pads of arrays of the cNT-on-Si post configuration were contacted with gold wire bonding and an anode made of a Pt mesh at 200 V bias was placed at about 2 mm from the sample. Purified hydrogen from a Pd diffusion cell was used in all the experiments.

3. RESULTS AND DISCUSSION

3.1 CNT-on-Si Post Emitters

Fig. 3 shows the anode current vs. gate voltage characteristics obtained first under UHV and then at 10^{-4} Torr of pure hydrogen from a 3840-cell array of the cNT-on Si post design (corresponding to Fig.1). The array was operated in an ion pumped UHV chamber for many hours before the UHV data were taken. Exposure to hydrogen increased the emission current by orders of magnitude and reduced the apparent "turn-on" voltage by 30%.

A separate array with the same number of cells was run overnight in a turbo-pumped chamber under a continuous flow of $1x10^{-7}$ Torr oxygen at a constant gate voltage of 50 V until the emission degraded to about 44 nA. The effect of the addition of a continuous flow of hydrogen at 9 x 10^{-5} Torr is shown in the anode current-time plot in Fig.4. A sharp increase in emission is followed by a gradual increase until stabilizing at 15 μA after about 2.8 hr, with an overall recovery factor of 340.

These results suggest that operation in oxygen did not (significantly) consume the nanotubes through reaction with oxygen to form CO or CO_2 gas. Instead, the emission degradation was likely due to surface contamination with oxygen, which was removed by reaction with hydrogen (atoms). We have observed that exposure of the emitters to molecular hydrogen or oxygen when the arrays were not emitting had no effect on the emission produced once the gases are removed. The fact that the emission characteristics do no change when exposed to gases unless field emission is taking place suggests that the nanotubes are inert to the molecular forms of hydrogen and oxygen and that the atomic forms, which are created by electron dissociation, react with surface groups either in removal or attachment processes.

3.2 CNT-in-Open Aperture Emitters

As reported previously [2], this configuration has achieved the lowest gate current to anode current ratio (2.5%) of any nanotube emitters to date. The results from a 40-cell array taken under UHV conditions are reproduced in Fig. 5.

Figure 6 compares the emission anode current from an array of 20 cells obtained under hydrogen pressures of $1x10^{-8}$ and $1x10^{-4}$ Torr in the UHV chamber. A large emission increase at the higher pressure was observed (i.e. a factor of 10 at 45 volts). The saturation behavior at higher voltages could be due to faster hydrogen desorption at the higher currents.

We did not observe significant changes in the emission current for hydrogen pressures below $1x10^{-5}$ torr. The effect increased with pressure up to about 10^{-4} torr, and stayed the same at higher pressures. The emission began to decrease as soon as the hydrogen was removed but some effect remained for several hours after the hydrogen was removed.

The requirement for relatively high pressures ($\geq 10^{-6}$ Torr) of hydrogen again suggests that atomic hydrogen is responsible for the large enhancement and regeneration effects and that atomic hydrogen is created by electron impact from the operating emitters. The production rate of atomic hydrogen is apparently too low at lower pressures.

The effect of the atomic hydrogen may be any or all of the following mechanisms a) chemical removal of oxygen-containing surface species (which may act as p-type dopants and/or increase the work function), b) formation of a surface dipole (reducing the work function), and c) n-type doping by atomic hydrogen.

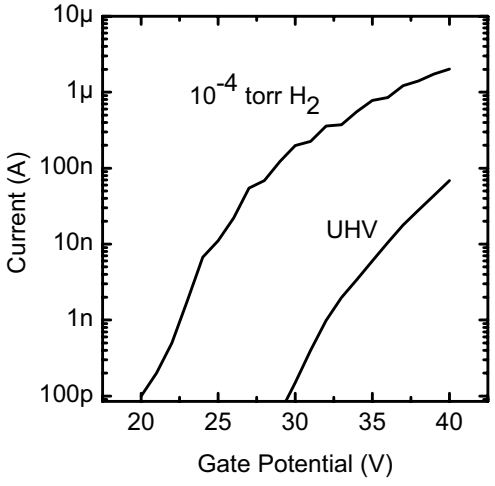

Fig. 3. Anode current- voltage characteristics of array of cNT-on Si post emitters obtained under UHV conditions and under 10^{-4} Torr hydrogen.

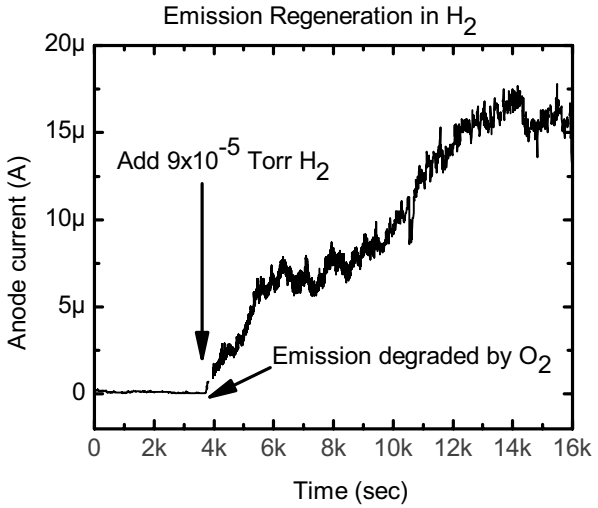

Fig.4. Anode current-time evolution showing regenerative effect of hydrogen on oxygen-degraded cNT-on-Si post emitters.

The results suggest that these beneficial hydrogen-nanotube interaction processes could also be accomplished and speeded up by exposing the emitters to an external source of hydrogen atoms. The inclusion of hydrogen at appropriate pressures (so not to affect electron mean free-path) in devices which use cNT emitters can enhance emitter lifetime and result in large cost-savings.

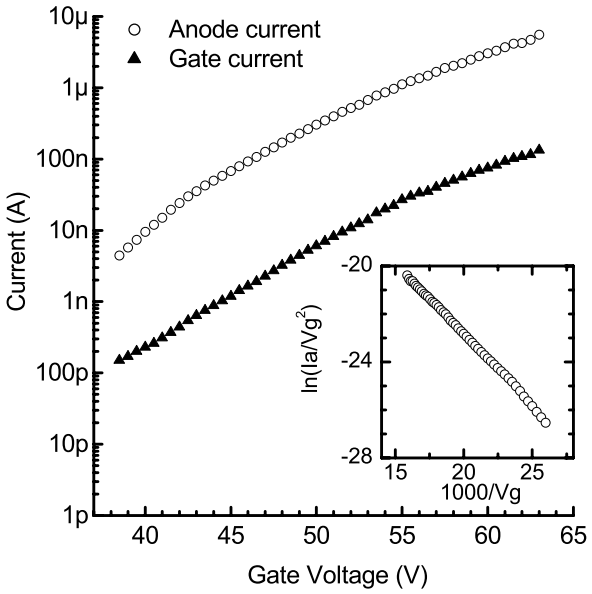

Fig. 5. Emission current-voltage characteristics from an array of 40 cells corresponding to Fig. 2. Inset shows a Fowler-Nordheim plot of the anode current, the linearity of which indicates well-behaved field emission.

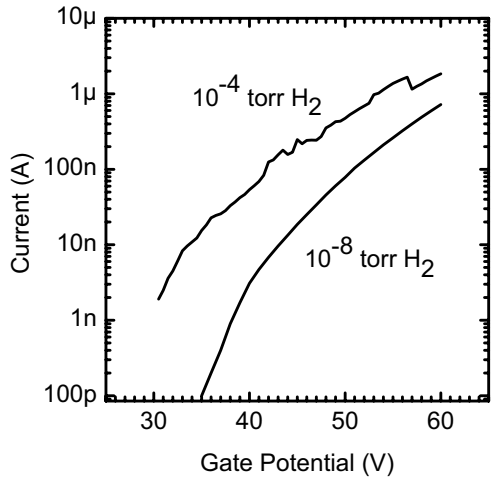

Fig. 6. Emission anode current - voltage characteristics from an array of 20 cells of the cNT-in-open aperture emitters obtained under 1 x 10^{-8} (lower) and 1 x 10^{-4} Torr (upper) hydrogen.

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