Electron beam stimulated field-emission from single-walled carbon nanotubes

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Carbon nanotubes are good candidates for electron field- and photo-emitters at the nanoscale since their sharp geometries lead to significant external field enhancement. Also, their mechanical strength and structural completeness alleviate issues related to stability and lifetime that may be present in small-scale emitters that have loose atoms at their tips. Here, we demonstrate how an external electron beam can stimulate electron emission from the tip of a nanotube that is lying on an insulating surface and is subject to an external electric field, thus making it act as an electron bombardment source. © *2004 American Vacuum Society.* [DOI: 10.1116/1.1809628]

I. INTRODUCTION

The large aspect ratio of carbon nanotubes (CNTs) leads to significant field enhancement at their tip when placed in an external electric field. This makes them very interesting candidates for field-emitters. Also, the mechanical strength and stability of CNTs suggest that they can provide large emission currents over substantial periods of time. If a CNT is subject to enough external field in a standard cathode–anode configuration, it acts as a normal field-emitter. Here, we investigate the question of how the electron emission process can be stimulated using another electron beam that hits the CNT. This electron beam can, for instance, be the primary beam of a scanning electron microscope (SEM).

II. METHODOLOGY

In normal SEM imaging, CNTs typically do not show particularly high secondary electron coefficients, even at their tips. In other words, an electron beam is not a sufficient driving force to create emission from the CNT in the presence of small external electric fields such as those generated by the secondary electron detector of the SEM. Therefore, another agent is needed in conjunction with the primary beam. This can be a strong external electric field. This field would not be strong enough to cause emission by itself, but would reduce the emission energy of the tube at the tip to a level that could be overcome with the action of the primary bombarding electron beam. Hence, we call the resulting emission process "stimulated field-emission" (SFE), i.e., field-emission that is stimulated by another electron beam.

In these experiments, we are interested in nanotubes that lie on a dielectric surface as opposed to freestanding vertical nanotubes. The advantage of the former is that they are fixed and their tip is not subject to much mechanical fluctuation. Thus, they can provide a more stable emission. However, because of the presence of the dielectric surface in their immediate proximity, external field enhancement around their tip would be less than in the case of freestanding nanotubes and they may require higher applied electric fields to emit.

III. DEVICE STRUCTURE

In order to apply the necessary external electric field easily without using high voltages, we need an extraction electrode very close to the CNTs under experiment. To avoid the difficulty of having to bring an electrode to very small distances from the nanotube, which requires very precise mechanical manipulation of a tip on the micron scale inside the chamber of the SEM, we integrated the extraction electrode into the emitter structure that was made using standard microfabrication techniques (Fig. 1). First, a step was made using lithography and dry etching of silicon—the extractor electrode was going to be placed at a lower level. Then came the growth of approximately 400 nm of wet thermal oxide on the wafer. Next, optical lithography was used to pattern all the electrodes, including the extractor, in photoresist. Approximately 50 nm of molybdenum was then sputtered onto the wafer and a lift-off in acetone completed the fabrication of electrodes. Catalyst islands were similarly patterned using lithography on PMMA (polymethylmetacrylate) as resist, deposition from solution, and lift-off. The catalyst contains alumina, iron, and molybdenum particles. Nanotubes were grown using chemical vapor deposition with methane and ethylene as source and hydrogen as carrier gases. Typical gas flow rates were 1000, 20, and 500 sccm for methane, ethylene, and hydrogen, respectively. The growth temperature was in the range of 850 to 900 °C, and the duration of the process was 5 min. This process is well known to produce single-walled carbon nanotubes.[1]

The experiments were carried out inside a Hitachi S-2500 SEM. An appropriate sample holder and custom-made feedthroughs had been added to the tool to enable the application of voltage to the devices inside the chamber.

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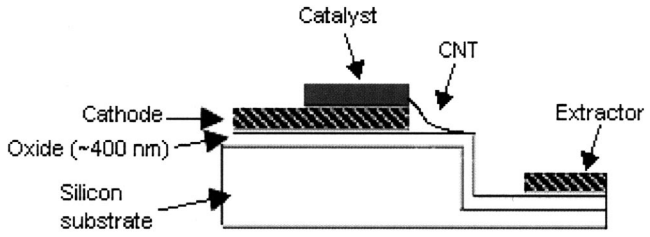

FIG. 1. Cross section of a device (thicknesses shown are not to scale).

IV. EXPERIMENT

In a typical experiment, the extractor gate was held at ground potential and a negative bias was applied to the cathode (the electrode that had the CNTs attached to it). By gradually increasing the value of the negative bias, we would first observe voltage contrast, i.e., negatively biased regions, including the nanotubes, would appear much brighter than other areas [Fig. 2(a)]. This is due to the enhanced secondary electron collection from these regions because of the negative bias. If the magnitude of negative bias was increased beyond a certain threshold value, there would be spontaneous field-emission from various places on the sample, including the nanotubes. The SEM video system would be saturated and the whole image would be lost in white signal. However, if the sample was biased very close to the onset of emission, but not quite into the spontaneous field-emission regime, the areas with great field enhancement that were ready to emit could be excited with the primary beam of the SEM. As a result, in this close-to-threshold regime, there would be field-emission from nanotube tips only when the primary beam hit them. Therefore, these points appeared as extremely bright spots on the SEM image [Fig. 2(b)].

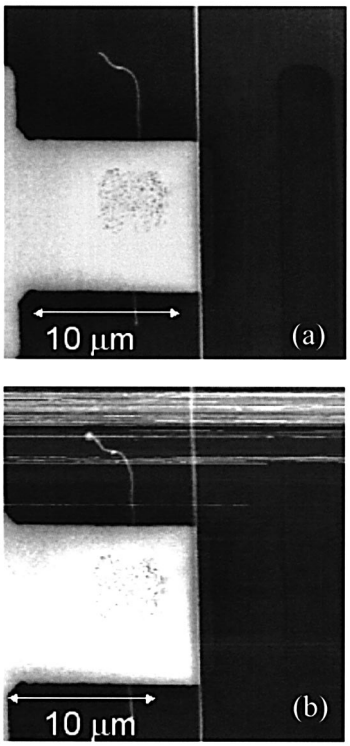

FIG. 2. (a) Voltage contrast. A voltage of −24 V is applied to the nanotubes with respect to ground (the gate electrode on the right). (b) Applied voltage is 25 V. Stimulated field-emission can be seen as a bright spot on the nanotube tip. The bias voltage is right at the spontaneous emission threshold, and some traces of spontaneous emission can be seen as white stripes on the top portion of the image. (Primary beam acceleration voltage: 5 kV.)

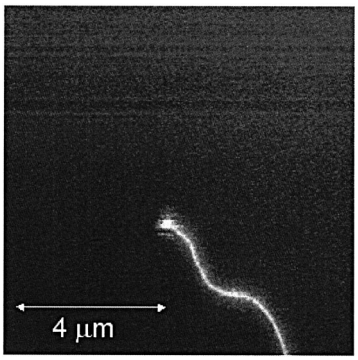

FIG. 3. Stimulated emission is observed even at very high magnification (small field of view), where only the region around the tip of the nanotube is scanned (no electrode or catalyst lies in the field of view). (Primary beam acceleration voltage: 5 kV.)

On some of the devices, rather than having only a few spots (nanotube tips) that exhibited significant external field enhancement, there were vast areas that started normal field-emission before emission from nanotubes. These could be, for example, sharp protrusions on catalyst islands. In these cases, stimulated field-emission from nanotube tips was not observed since the image was lost due to spontaneous field-emission. We obtained stimulated field-emission from tube tips on almost 70% of the samples.

V. RESULTS AND DISCUSSION

Below a certain magnification (usually on the order of ~1000), stimulated field-emission would disappear. At constant scan time (TV scan), reduced magnification means faster motion of the beam, and, as a consequence, less charge delivered to each point on the sample. At very high magnification, which means a very small field of view (only limited to the area around the tube tip), stimulated field emission still existed (Fig. 3). So, the phenomenon was not due to charging of other places (electrode and catalyst that were connected to the nanotubes) from the primary beam, but was from the interaction of the primary beam directly with the CNT tip area.

Typically, the primary beam current was a few picoamperes. On one of the samples, the experiment was performed at constant magnification in a relatively large range of primary beam currents, starting at 2.4 pA, and going down to ~0.7 pA (primary beam energy: 5 kV). Surprisingly, stimulated emission was still observed at low current on some of the CNTs. At much lower primary beam currents (a few tens of femtoamperes), where it was very hard to even obtain an image of the sample, at very slow scans, the tube tips still exhibited significant brightness compared to the rest of the samples (the body of the nanotubes was almost invisible at

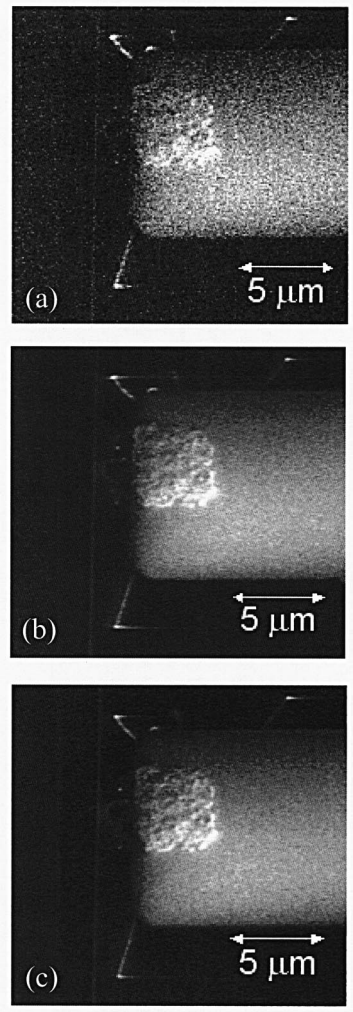

FIG. 4. Stimulated field-emission under various video sample averaging methods: (a) point by point; (b) line by line; (c) frame by frame. Applied bias: −49 V. Number of samples averaged: 32. (Primary beam acceleration voltage: 3 kV.) Note that in line or frame modes, the streaks emanating from nanotube tips are longer than in the point mode.

this low current). We observed stimulated field-emission at primary current levels and slow scan times that corresponded to the delivery of only a few electrons to each square nanometer of the sample, which is the approximate size of the nanotube tip area.

There are various methods of averaging video signal samples to reduce the noise level (point by point, line by line, or frame by frame) for an image capture. If the emission lasts for a while after the primary beam has swept past the nanotube tip, the collected electrons (still being emitted from the nanotube) by the SEM detector will be attributed to the new places being scanned. As a result, streaks will appear on the image, originating from nanotube tips. This was indeed the case in some of the experiments. If image averaging was done line by line or frame by frame rather than point by point, the stripes were longer since in these cases the primary beam was moving faster (Fig. 4).

On a given structure, not all the nanotubes showed the same amount of brightness at their tips. Also, some of them

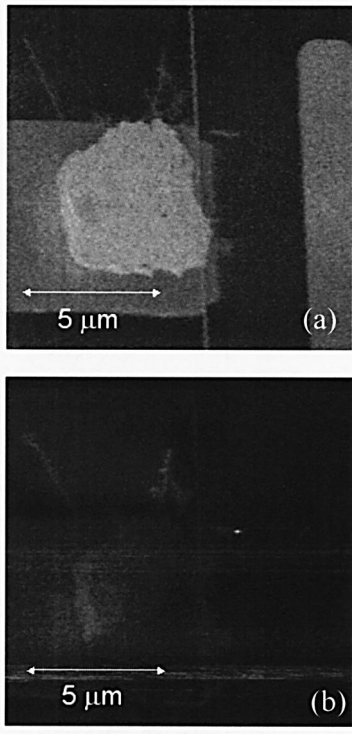

FIG. 5. Imaging and stimulated field-emission at a low primary beam acceleration voltage of 500 V. (a) Zero bias—normal SEM image; (b) applied bias is −30 V. Note that stimulated emission is hard to obtain at this low value of primary beam acceleration voltage, and only one of the nanotubes exhibits the phenomenon.

required higher external fields to exhibit SFE. This could be related to the tube tip structure, i.e., its being capped or open, terminated with other atoms from the environment, and so on. It is known that these various types generate different levels of external field enhancement.[2]

SFE was observed at primary beam acceleration voltages ranging from 3 to 20 kV. At 2 kV and below (the experiment was done at 2 kV, 1 kV, and 500 V), SFE was very hard to obtain on most of the nanotubes, even though the nanotubes were observed clearly (Fig. 5). In one experiment, we started at 5 kV primary acceleration voltage, where stimulated field-emission was very easily obtained [Fig. 6(a)]. We then proceeded to reducing the acceleration voltage: At 3 kV, the effect was relatively easily obtained. At 2 kV, we did not see any SFE. At 1 kV, SFE was very hard to observe, and at 500 V, although slightly stronger than at 1 kV, it was still very hard to obtain [Fig. 5(b)]. Interestingly, different nanotubes exhibited SFE at 3 kV (not shown) and 500 V. Weak SFE at low primary beam acceleration voltages could be due to the primary electrons not having enough energy to initiate the process. Oxide charging can provide another possible explanation: a negative charge accumulation in the oxide as the result of illumination by the primary beam may provide the energy needed by the electrons in the tube tip to overcome the emission barrier. Thus, at lower primary acceleration voltages that approach the oxide charging crossover point, or below that where there is no oxide charging or even positive charging, there would be no

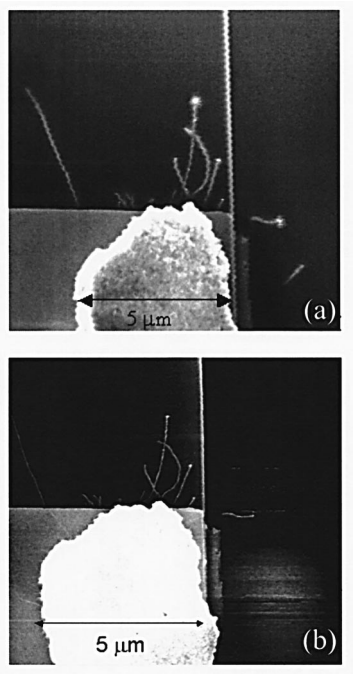

FIG. 6. Stimulated field-emission at high primary beam acceleration voltages: (a) 5 kV; (b) 20 kV. SFE was easiest to obtain at around 5 kV.

stimulated emission. In order to test this hypothesis, we needed to isolate the effect of oxide charging from the lowering of the primary beam energy. High acceleration voltages provided just such an occasion. Since the thickness of the oxide layer underneath the tubes is only about 400 nm, at primary beam energies higher than about 5 keV, the penetration of electrons creates a so-called electron-beam-induced-current that circulates between the oxide surface and the conducting silicon substrate below it. Therefore, there is no accumulation of charge at the surface. There might even be positive charge accumulation as discovered by Bai *et al.*[3] However, we observed SFE at primary beam energies of up to 20 kV [Fig. 6(b)]. This indicates, at least, that oxide charging is not the only root cause of SFE. Nonetheless, the phenomenon is most pronounced at 5 kV, where the amount of oxide charging for the thickness in question is around its maximum negative value. So, charging may be one of the players in the event.

If oxide charging is not the main driving force of SFE, there must be direct energy transfer from the primary beam to the electrons in the nanotube tip. However, the nanotube tip is a very small volume (on the order of 1 cubic nanometer), and the primary electrons will not have a chance to undergo scatterings with multiple nanotube electrons. Therefore, it is hard to explain the high number of emitted electrons generated by this process (as suggested by the extremely bright emission spots) based on the same model as a bulk electron bombardment source. We suggest a different qualitative model: Due to the extremely strong field enhancement at the nanotube tip, a high number of nanotube electrons are attracted to the tip area. Once a primary electron hits the tip, it interacts with a large number of them simultaneously. This type of interaction may be fundamentally different from the two-particle scattering that primaries hitting a bulk material undergo a number of times. Therefore, the characteristics of the emitted electrons may be different from normal secondaries emitted from bulk materials, e.g., there may be special phase relations among the electrons emitted as a result of each primary incursion. One problem in doing these experiments was that, especially in the poor vacuum conditions of $\sim 10^{-4}$ Torr in our chamber, the sample was subject to degradation due to e-beam-induced material deposition. So, the order of experiments performed on a sample (change in the primary beam energy, primary beam current, scan rate, and so on) could affect the outcome. Therefore, one needs to exercise caution in interpreting the results, and it is only by performing the experiments on multiple samples that conclusions are drawn on an average basis. The other option would be to have a multitude of samples of significant similarity (same quality catalyst island, same length and positioning of nanotubes, as well as same chiralities and diameters), which is almost impossible with the existing fabrication techniques. Future work will include performing the experiment under higher vacuum conditions to reduce sample degradation and improve sample lifetime and experiment repeatability, as well as measurements of the emission current and developing a qualitative model to describe the phenomenon.

VI. CONCLUSION

Electron beam-stimulated field-emission from single-walled CNTs was observed. The evidence suggests that the main mechanism behind the phenomenon is direct interaction of the primary beam with the nanotube rather than the charging of the surrounding oxide. The effective secondary electron emission coefficient is estimated to be at least 100.

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[1]J. Kong, H. Soh, A. Cassell, C. F. Quate, and H. Dai, Nature (London) **395**, 878 (1998).
[2]S. Han, "Theoretical study on the field emission of carbon nanotubes," Ph.D. dissertation, Seoul National University (2000).
[3]M. Bai, "Insulator charging in electron beam lithography," Ph.D. dissertation, Stanford University (2003).