

Scanning electron microscopy of field-emitting individual single-walled carbon nanotubes

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Carbon nanotubes are promising electron emitters because of their sharp geometries that lead to significant external field enhancement, as well as their mechanical strength. However, distinguishing the emission due to an individual single-walled carbon nanotube (SWCNT) from that due to surrounding structures is a challenge. Here, we demonstrate how a scanning electron microscope (SEM) can be used to view the emission from individual SWCNTs by applying an external field close to the onset of field-emission and then scanning the tube with the electron beam of the SEM. The stimulated emission is revealed in the SEM image as localized bright spots. © 2004 American Institute of Physics. [DOI: 10.1063/1.1763984]

Carbon nanotubes (CNTs) are very sharp and mechanically strong structures. Therefore, they are particularly appealing as candidates for micro- and nano-scale electron emitters. Since individual CNTs are very small and usually exist side by side with additional structures such as neighboring CNTs or metal electrodes on a substrate, it is often difficult to isolate the role that they play in a particular experiment from the effect of the surrounding structures. Electron emission is not an exception. In order to study the emission of an individual single-walled carbon nanotube (SWCNT) that is the active part of an electron gun microstructure, we must ensure that the observed electron beam is from only the SWCNT in question, and not, for instance, from sharp protrusions on metal electrodes, catalyst islands that constitute parts of the overall system, or neighboring CNTs. This problem is not exclusive to nanotube-based emitters, but can exist in any micro- or nano-structured electron emitter. Here it is demonstrated how a scanning electron microscope (SEM) can be used to view the emission sites ("hot-spots") of a nanotube field-emitter.

The electron beam of a SEM can deliver resolution of a few nanometers. So, the question is to obtain a suitable contrast mechanism for viewing field-emission sites. Figure 1 shows a scanning electron micrograph of a nanotube sample with zero bias applied to the electrodes that are connected to the nanotubes. As the bias is increased we see voltage contrast; that is, the negative regions appear brighter due to the enhanced collection of secondary electrons and vice versa. If the bias is increased slowly there may well be a region just below the emission threshold where an external agent such as a SEM beam is necessary and sufficient to provide the extra energy needed to stimulate the field-emission process, in which case the emission sites will appear as bright spots. Beyond that bias region there will be spontaneous field-emission (emission independent of the position or even existence of the primary beam) and the whole image will ap-

pear extremely bright since the field-emitted electrons will continually saturate the electron detector. Accordingly we built the structure of Fig. 1 and examined it in the SEM under different bias conditions.

The fabrication process included thermally growing about 400 nm of dry oxide on a silicon substrate. Molybdenum electrodes were formed by lithography, sputtering, and lift-off. A similar process was used to define the catalyst islands that contain iron, molybdenum, and alumina particles. The use of this catalyst is well established for the growth of SWCNTs.¹ The nanotubes were grown using chemical vapor deposition (CVD) for 5 min at 850 °C with methane and ethylene as precursors and hydrogen as a background gas. The flow rates were 1000, 15, and 500 (all in sccm), respectively. Under these low-yield conditions in our CVD chamber, frequently, as here, only one of the catalyst islands formed a significant number of CNTs. The sample was then mounted in a Hitachi S-2500 SEM with custom

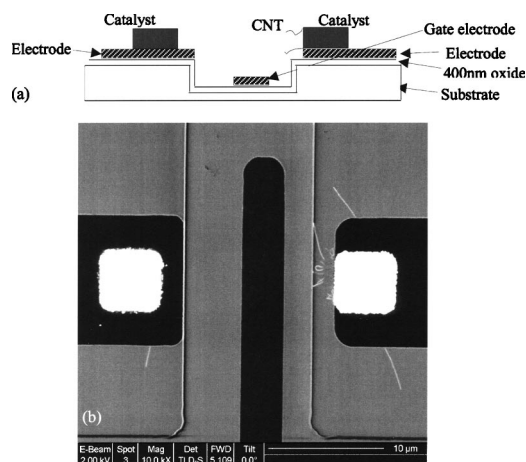


FIG. 1. (a) Cross-sectional schematic view of the structure. (b) SEM image taken in an FEI Strata dual beam system (normal incidence). Several nanotubes are connected to the electrode on the right, but there is only one nanotube attached to the electrode on the left. The extractor gate can be seen in the middle of the structure, in a 1- μ m deep trench.

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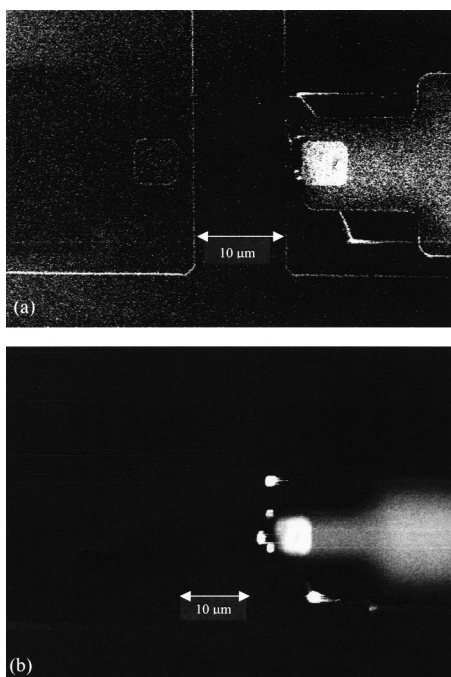


FIG. 2. (a) The device image (normal incidence) under an applied -71 V bias (to the right electrode) in a Hitachi S-2500 SEM (acceleration voltage: 3 kV). Note: the emission threshold had already shifted to this value at the time this image was taken. (b) Similar to (a), but the emission threshold was about -78 V in this case.

feedthroughs and sample holders to apply bias to the electrodes.

In a first experiment the extraction gate (middle) and the right electrode were held at zero potential and a negative voltage was applied to the left electrode. In the second experiment the roles of the left and right electrodes were interchanged; the left electrode and the gate were held at zero potential, and a negative bias was applied to the right electrode. Thus we might expect the bias required for field emission in the first experiment to be higher than that in the second case because of the scarcity of CNTs on the left-hand electrode.

This was indeed the case. In the first experiment the bias had to be increased to -120 V before field emission started, and the whole SEM image was washed out presumably because of the large number of emitted electrons from numerous locations on the catalyst island and electrode, saturating the electron detector independently of the position, or even presence, of the SEM beam. In the second experiment, field emission was first obtained at a bias voltage of about -40 V. Although the electric field is enhanced at the tips of the nanotubes, this corresponds to an average field of about 8 V/ μm , which is approximately the value that has been reported previously for nanotube field emission.² More important, at the onset of emission, the SEM image did indeed, as speculated, exhibit a few bright spots corresponding to the positions of the CNT tips (Fig. 2). This image could be unstable since small fluctuations in the applied bias or emission threshold could lead to a full-scale spontaneous emission and washing out of the image. The emission stopped after a few minutes (presumably due to the degradation of the sample because of carbon deposition in the poor vacuum environment), and in order for it to restart, a higher negative voltage (-50 V) was needed. Again we saw the same “hot spots,”

and then emission decreased and eventually disappeared after a few minutes, and could be obtained again at progressively higher negative values of bias voltage on the right electrode.

Note that these bright spots are due to stimulated field emission and not just voltage contrast. Voltage contrast affects all the negatively biased regions in a uniform manner and increases rather linearly with voltage. On the other hand, the appearance of the bright spots happens suddenly and only in a small voltage range (a few tenths of a volt) before the spontaneous emission regime. Also, it is observed that as the field of view in the SEM image is increased to beyond a certain level, the bright spots disappear even though voltage contrast still exists. This is because a larger field of view indicates a smaller primary beam density at each location—an amount that may no longer be enough to provide the necessary stimulation. In order to obtain this stimulated emission at the level observed in Fig. 2(a), a SEM beam current of 2.5 pA and a slow scan rate of 8 ms/line was necessary. We have not as yet been able to measure the stimulated emission current because of large interelectrode leakage currents on our devices, but the existence of white tails and stripes emerging from the bright spots is an indication of the saturation of the detection system that lasts for a certain period of time. This suggests that the emission current is much higher than our primary beam current (2.5 pA in this case). Based on the scan rate for this particular image, the time duration of the bright tails in Fig. 2(a) can be estimated at about 1 ms. This can be either due to the time response of the detection system itself, or a sign that emission from the hot spots lasts for some time even after the primary beam has swept past them.

In order to support the idea that the bright spots (i.e., stimulated emission sites) are primary emitting areas even in the spontaneous emission regime, we present the following arguments: First of all, one can expect that the sharp nanotube tips exhibit more field enhancement and lower emission thresholds than other regions (field enhancement at the tip in the case of a free-standing nanotube has previously been reported³); the experimental result is consistent with this expectation. Moreover, as mentioned previously, no emission at similarly low values of bias was obtained from the left electrode, which is largely barren of nanotubes. Also, as expected, the spontaneous emission starts at biases just higher than those for stimulated emission such as in Fig. 2 (the experiment was repeated several times, with very reproducible results); if other regions were primarily responsible for spontaneous emission, we would not always see these bright spots exactly at the onset of emission.

There can be a number of possible mechanisms for this stimulated field emission. Note that the bias voltage in Fig. 2 is almost at the threshold of emission, and only a small energy transfer to the electrons that are ready to emit is sufficient to drive the areas with high field enhancement to the emission regime. One possibility is that the primary beam electrons directly transfer energy to the electrons that are ready to emit from the tube. Another explanation is based on oxide charging. A little surface charge induced in the oxide underneath the nanotube tip by the scanning electron beam can provide the extra electric field that is needed to start the process of field emission. The emission lasts only as long as the induced charge has not leaked away. Thermal effects may be another possibility. If we assume that all the energy from

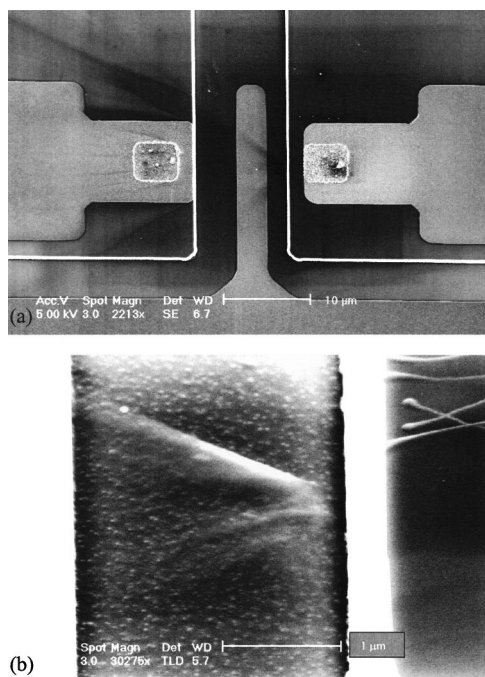


FIG. 3. Images of the sample after emission experiments. (a) Normal incidence. (b) At a 50° tilt with higher magnification [the region shown corresponds to the region between the right and middle electrodes in (b)]. Radial patterns from carbon deposition by the field-emission beam have a center around the nanotube tips. The offset between these two regions in (b) is due to the 50° tilt of the sample. Note that the tips of the tubes have grown larger as a result of emission. Images were taken in an FEI Sirion SEM (acceleration voltage: 5 kV). The small white dots seen above the right electrode in (a) were added by selective carbon deposition after field-emission experiments on this sample.

the primary beam is transferred to the tube tip and we use a rod of 1 nm in diameter and $1 \mu\text{m}$ in length as a model for a nanotube, the induced temperature increase due to the primary beam (3 keV acceleration voltage and 2.5 pA current) would be about 0.75 K, which is too small to be a possible reason for stimulated emission. So, unless there is a peculiar local heating of the tip atoms by the primary beam, thermal effects do not seem to be at the root of the stimulation. We are currently working on understanding these mechanisms in more detail and finding out which one is dominant in a particular experimental configuration.

In a final experiment the sample was imaged following the field-emission experiments (Fig. 3). Black radial patterns were observed emanating from the emission point toward the extractor electrode. These patterns that did not exist prior to the emission experiments can be attributed to carbon deposition from the breakdown or surface migration of residual hydrocarbons by electrons. This is yet another indication that field emission is taking place from the bright areas at the tips of the nanotubes in Fig. 2, and this is why the center of these radial patterns is in that region. Furthermore, the tips of the nanotubes responsible for emission are enlarged, possibly due to carbon deposition from residual gases [Fig. 3(b)]. We have inspected the endings of non-emitting nanotubes in other areas of the sample and they do not exhibit enlargement of the tips.

In conclusion, a SEM can be used to map the electron emission of a cathode containing carbon nanotube field emitters. Although used for nanotube-based emitters in our experiments, the technique may also be used in imaging other types of micro- or nano-structured emitters. Also, on a sample with vertically aligned nanotubes like those considered for flat panel display applications, by placing an electrode in the proximity of the tubes to provide the external field, it is possible to perform similar experiments. In these preliminary experiments the limits of resolution were not determined but at least the emission for individual SWCNTs was easily resolved. We are working on fabricating new structures with lower leakage currents, as well as improving the imaging resolution and finding out more about the physical mechanism of beam-stimulated field-emission.

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