Cutting of carbon nanotubes assisted with oxygen gas inside a scanning electron microscope

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The authors report a cutting technique for carbon nanotubes (CNTs) assisted by the presence of oxygen gas. The cutting procedure is conducted in less than 1 min using a low-energy electron beam inside a scanning electron microscope. The oxygen gas was regulated by a mass flow controller and was injected at 1 SCCM. It was found that although the total pressure inside the specimen chamber reached 10^{-2} Pa, high-speed cutting occurred only in an area close to the oxygen gas nozzle. They assume that the CNTs are cut only under a low acceleration voltage since the CNT molecules are easily excited and ionized by the low-energy electron beam. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2348779]

As a typical nanomaterial, carbon nanotubes[1] (CNTs) have interesting mechanical, electronic, and chemical properties which have been under investigation in various studies for over a decade. Recently, nanotubes have been proposed as a basic building block for the next generation of nanoelectronic and mechanical systems. In prior studies, CNTs have been used as linear and rotational nanobearings,[2,3] mass conveyors,[4] field emitters,[5,6] atomic force microscope (AFM) probes,[7] nanotweezers,[8] and nanoposition sensors.[9] The CNT length is an important parameter for the fabrication, manipulation, and assembly of nanotubes, since it influences the function and the structure of nanodevices and nanostructures. It is significant to be able to produce nanotubes with specific lengths.

A number of methods for cutting nanotubes have been investigated previously. Peeling and sharpening of multiwalled carbon nanotubes (MWCNTs) through electrically driven vaporization presented the possibility for the removal of layers.[10] However, this method is difficult to control and requires the electrode to be in electrical contact with the CNTs. Cutting and removal of CNTs at a nanometer- and even an angstrom-scale using a high-energy electron beam within a transmission electron microscope (TEM) was reported by Banhart and co-workers.[11,12] Although the use of a TEM allows CNTs to be cut at high resolution, the typical small size of the specimen chamber makes it difficult to use it for nanofabrication processes and for the assembly of nanodevices inside a TEM. In addition, in a destructive fabrication technique for breaking CNTs, the location of the damaged site is unknown and is difficult to control.[13] Other mechanical cutting methods involving an AFM (Ref. 14) or a scanning tunneling microscope tip[15] are time consuming. Cutting using a focused ion beam can damage the rest of the nanotube.[16]

Electron beam irradiation-induced damage on CNTs under a low acceleration voltage inside a scanning electron microscope (SEM), followed by annealing of the nanotubes in air for selective removal, was reported.[17] *In situ* cutting of CNTs in the presence of water vapor inside an environmental SEM has been reported by Yuzvinsky *et al.*[18] The study revealed mass loss of the CNTs caused by water molecules. Highly reactive OH, H, and HO_2 radicals can react with carbon atoms to form CO and CO_2, resulting in mass loss from the CNTs. However, none of these previous studies has explained why CNTs can be cut using low-energy electron beams. It is known that in order to remove a carbon atom by a knock-on collision, a minimum incident electron energy of 86 keV is required.[19] Such a high-energy beam can be easily obtained inside a TEM. However, in a SEM, the energy of the electron beam is normally limited to 30 keV. The cutting mechanisms inside a SEM will therefore be very different from those inside a TEM.

Here, we present a technique for high-speed cutting of CNTs in a SEM by introducing oxygen gas into the vicinity of the sample, and we explain why cutting occurs only under a low-energy electron beam.

Multiwalled carbon nanotubes with 20–50 nm diameters were synthesized by the standard arc-discharge method. We fixed a bundle of CNTs on a stage using electrically conductive tape. Oxygen gas (purity of 99.999 95%) was introduced into the vicinity of the sample through a glass nozzle with a 20 μm opening at the end and was regulated by a digital mass flow controller. The CNTs were observed using an acceleration voltage of 5 kV and cut normally using 1 kV inside a field emission SEM (FESEM, JEOL JSM-6500F). We selected the spot mode of the electron beam to cut the CNTs. The vacuum in the specimen chamber was reduced from 10^{-4} to 10^{-2} Pa when oxygen gas was introduced at 1 SCCM (SCCM denotes cubic centimeter per minute at STP). In order to observe clearly where the cutting occurs on a CNT, TEM images were taken before and after the cutting

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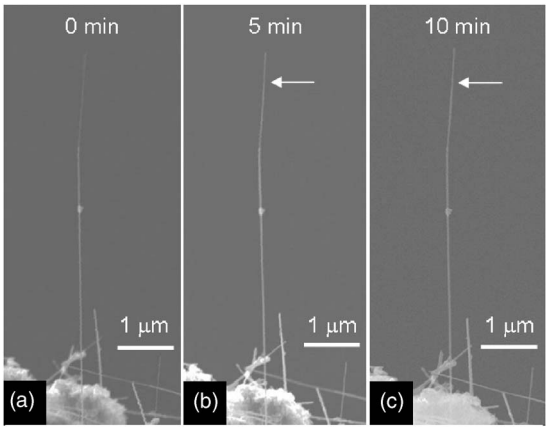

FIG. 1. Single CNT exposed to an electron beam without the presence of oxygen gas. No changes in the CNT were observed. The beam exposure times are (a) 0 min, (b) 5 min, and (c) 10 min.

process in a JEOL 2100 TEM using an acceleration voltage of 200 kV.

A nanorobotic manipulation system with 16 degrees of freedom was used for three-dimensional manipulation of the CNTs. The manipulator is actuated by Picomotors™ (New Focus Inc.) for coarse motion and piezoelectric transducers for fine motion and is operated inside the FESEM. The resolutions of the manipulators are better than 30 nm (linear) and 2 mrad (rotary) for coarse motion and within nano-order for fine motion.[20,21] We used a nanorobotic manipulator to adjust the gap between the nanotubes and the gas nozzle in this study.

We show three sets of results for the cutting technique under different conditions. One is for irradiation of a CNT with a low-energy electron beam in the absence of oxygen. The second is by irradiation of a CNT with the introduction of oxygen gas when the gas nozzle was 1 mm from the samples. Finally, we show the cutting of a single CNT at high speed in the presence of oxygen and with the gas nozzle at 90 μm from the samples.

A single CNT was irradiated with an electron beam current of 6×10^{-10} A, an acceleration voltage of 1 kV, and in the absence of oxygen. The vacuum in the specimen chamber was 2.7×10^{-4} Pa. The electron beam was irradiated in a spot mode in an area 500 nm away from the tip of the CNT.

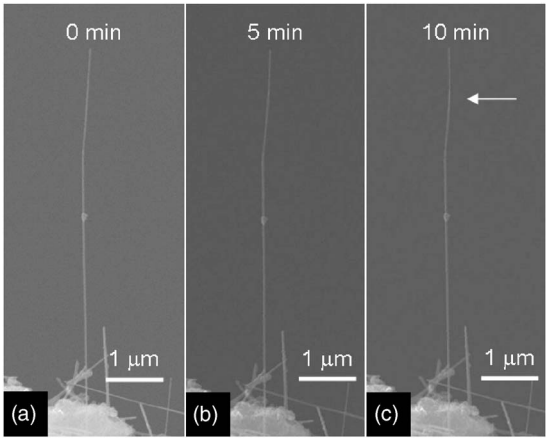

FIG. 2. Single CNT exposed to an electron beam with the introduction of oxygen gas. In this case, the nozzle is far from the cutting object. The results of irradiation after (a) 0 min, (b) 5 min, and (c) 10 min are shown.

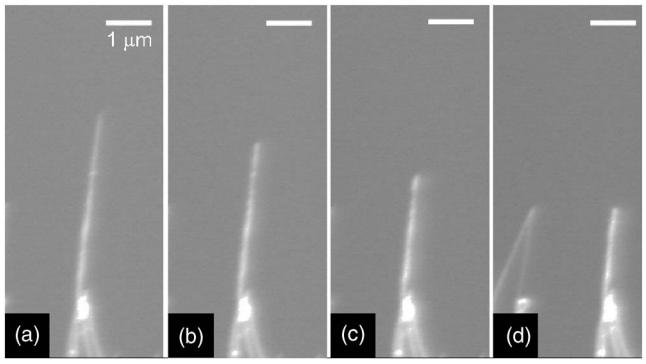

FIG. 3. (a) Before and [(b)–(d)] after cutting of a single CNT in less than 1 min. (b) A length of 650 nm was cut off the first time, (c) a further 700 nm was cut off the second time. (d) The CNT on the right after cutting has the same length as the one on the left.

The results of irradiation after 0, 5, and 10 min are shown in Figs. 1(a), 1(b), and 1(c), respectively. No variation in the appearance of CNT was observed.

Next, 1 SCCM oxygen gas was introduced in the specimen chamber, and the gas nozzle was located 1 mm from the samples. The total pressure in the specimen chamber reached 1.6×10^{-2} Pa. The irradiated point was 500 nm away from the tip of the CNT. Irradiation times were 0, 5, and 10 min, as shown in Figs. 2(a), 2(b), and 2(c), respectively. It can be observed that there was no significant change in the appearance of the CNT except for a small bend at a 4° angle after 10 min [see Fig. 2(c)]. However, the nanotube was not cut in this case.

In the third case, a single CNT was cut by the electron beam in the presence of oxygen gas, as shown in Fig. 3. Cutting was performed using the same electron beam current and acceleration voltage as the two previous cases. The vacuum pressure was 1.6×10^{-2} Pa and the oxygen gas flow rate conditions were the same as previously; however, the nozzle was located at a distance of 90 μm from the CNT in this case. Figure 3(a) shows the CNT before cutting, Fig. 3(b) shows the CNT after a length of 650 nm has been cut off, and Fig. 3(c) shows the CNT after removing a further 700 nm. Figure 3(d) shows the cutting of a CNT such that it has the same length as the one on the left. These experimental results demonstrate that the length of CNT can be pre-

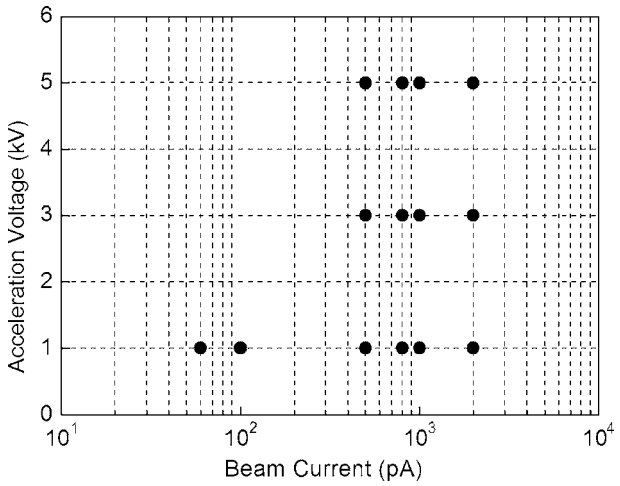

FIG. 4. Cutting of CNTs in less than 1 min under various acceleration voltages and beam currents shown by the black circles.

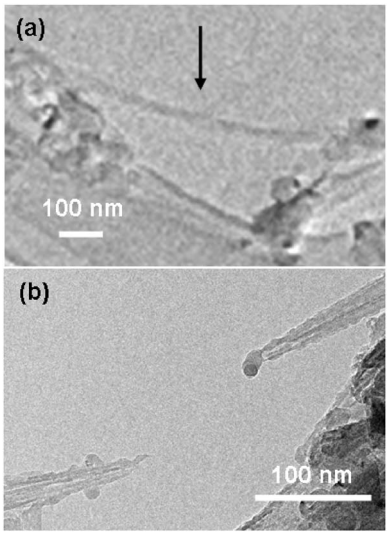

FIG. 5. TEM images of MWCNTs (a) before and (b) after cutting. It was estimated that about 100 nm of material was removed.

cisely controlled by cutting using an electron beam, assisted with oxygen gas. The acceleration voltages and the beam currents that can cut CNTs in less than 1 min are shown in Fig. 4. Cutting is easy and rapid at low acceleration voltages and high beam currents.

As shown by the experimental results, two conditions are required for CNT cutting. One is a low-energy electron beam damaging the CNT and another is the presence of oxygen gas that reacts with carbon molecules to form CO and CO_2. The cutting process requires a low-energy electron beam probably because the ionization of carbon molecules is independent of the energy of the primary electrons. The ionization efficiency is a maximum when the irradiation beam energy is three or four times larger than the core-electron binding energy. The core-electron binding energy of carbon is 290 eV.[22] The irradiation beam energy is 870–1160 eV, which allows us to obtain the maximum ionization efficiency readily. Secondary electron yields are obtained at a maximum of 300–1100 eV.[23] Carbon molecules are easily excited and ionized under a low acceleration voltage ($\sim$1 kV). We have only demonstrated these phenomena at acceleration voltages from 1 to 30 kV because the SEM cannot be operated at less than 1 kV.

The second experiment described above reveals that the oxygen gas has an uneven distribution even though the nominal pressure in the specimen chamber was 10^{-2} Pa. For cutting CNTs in less than 1 min, the gas nozzle needs to be close to the sample. In our case, the gap between the CNTs and the gas nozzle was less than 100 μm. If this gap is increased, the amount of oxygen available to react with the CNTs will decrease, thereby increasing cutting time.

However, what is the influence of the beam irradiation-induced heating on the cutting of the CNTs? We can estimate the increase in temperature ΔT induced by electron beam irradiation at the point model from the following equation:[24]

$$\Delta T = 0.48 E_0 I_p / kd,$$

where E_0 is the acceleration voltage, I_p is the irradiation current, k is the thermal conductance of CNTs, and d is the diameter of the beam. In our experiment, $E_0 = 1$ kV, $I_p = 0.6$ nA, and $d \approx 3$ nm. The value of k is 3500 W m^{-1} K^{-1}.[25] ΔT is then calculated to be 0.027 K. The increase in temperature is sufficiently small that its influence on the cutting of CNTs can be ignored.

Figure 5 shows nanotubes deposited on a TEM grid before and after cutting. Figure 5(a) shows a nanotube suspended across a gap before cutting. The cutting was performed inside a SEM in 1 min. Figure 5(b) shows that the CNT was cut and about 100 nm of material was removed. The gap is larger than the beam spot size of 3–5 nm, and the tips of the cut CNT are sharpened. The main reason for this is the drift of the electron beam.

In conclusion, we have demonstrated that CNTs can be cut in less than 1 min under a low acceleration voltage assisted by the presence of oxygen gas inside a field emission scanning electron microscope. Oxygen gas was regulated by a mass flow controller and introduced with a gas nozzle. It is found that although the total pressure in the specimen chamber reached 10^{-2} Pa, cutting at high speeds only occurred in an area close to the gas nozzle. We assume that the cutting of a CNT requires a low-energy electron beam, since the ionization efficiency is high at low primary electron energies. The electron beam induced heating can be ignored during the cutting process since it is small. We expect that the *in situ* cutting technique demonstrated here will be widely used for rapid prototyping of CNT nanodevices.

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