Manipulation of Carbon Nanotubes inside Field-Emission Scanning-Electron Microscope

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We demonstrate a new approach for manipulating nanostructured materials inside field-emission scanning-electron microscope (FE-SEM). We have installed two nanomanipulators inside FE-SEM which can travel about 20 mm with a minimum increment of 1 nm. Both render the motion in x, y, and z directions, providing various manipulation freedoms such as moving, bending, cutting, and biasing. We carried out *in situ* characterizations of electron beam-induced junction between the W tip and carbon nanotubes. A simple operation of fabricating a carbon-nanotube transistor on pre-patterned metal electrodes will be also demonstrated.

Various nanostructured materials such as CdSe, TiO_2, Si nanowires, and carbon nanotubes (CNTs) have been successfully produced by controlling the size of constitute elements and building blocks.[1-4] These nanostructured materials show unique electrical, optical, and physical properties compared to bulk because of the size, shape, and surface chemistry. For instance, CdSe nanoparticles can exhibit any color in spectrum simply by modulating the size of particle.[5,6] In addition, carbon nanotubes can be a metal or a semiconductor depending on their diameter and chiral angle.[7,8] These nanostructured materials have opened a new possibility for applications to medicine, memory devices,

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energy storage, displays, and so on. However, one of the most difficult challenges in this field is the various nanomanipulations such as positioning, transporting, and fabricating nanomaterials into a desired form of devices, which generally requires a tremendous effort because of the small dimension. Therefore, a new manipulation technique with high precision and maneuverability should be developed if possible.

Several methods have been attempted in order to access and manipulate nanostructured materials.[9-12] Manipulation inside transmission electron microscope (TEM) is advantageous because of the availability of diverse microscopies such as electron diffraction pattern and electron energy loss spectroscopy (EELS) in atomic resolution, but TEM is not easily accessible. Atomic force microscope (AFM) and scanning tunneling microscope (STM) are also feasible to manipulate even a single atom. These microscopes, however, should scan the substrate first to locate the target materials and must be switched into manipulation mode for subsequent operations. Furthermore, this approach sometimes accidentally damages the target materials while approaching to the materials due to thermal or mechanical vibrations.

In this report, we used field-emission scanning-electron microscope (FE-SEM) in order to monitor the movement of two manipulators. The primal advantage of the FE-SEM comes from high resolution and long working depth, which is unobtainable from the state of the art optical microscope. Our FE-SEM (JEOL, JSM-6700F) has a maximum resolution of 1 nm at 15 kV. Inside the FE-SEM, we have integrated two nanomanipulators (Klocke Nanotechnik, Aachen; www.nanomotor.de) made of piezoelectric materials.[13] Each manipulator is designed to travel up to about 20 mm with an accuracy of 1 nm and 5 mm/sec at full speed. This manipulator is small enough to fit into the space between the sample stage and magnetic lens so that it can travel to several millimeters over the sample in vertical direction. What makes the manipulation more adaptable for diverse operations is that we can mount various tools at the end of manipulators. We shielded the manipulators with a metal housing to prevent them from being charged. The detailed configuration of our system is schematically shown in Fig. 1(a).

For the manipulation, we have inserted electrochemically etched polycrystalline tungsten wires into the end of nanomanipulators, as shown in Fig. 1(b).

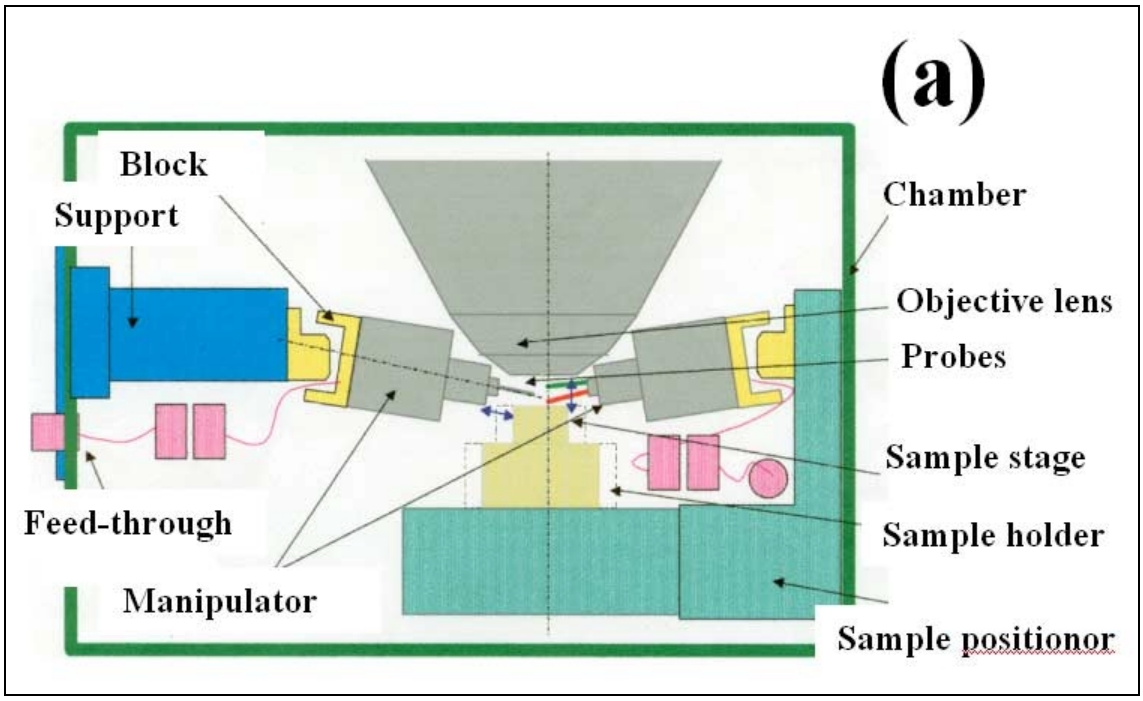

FIG. 1. (a) Block diagram of FE-SEM and two manipulators.

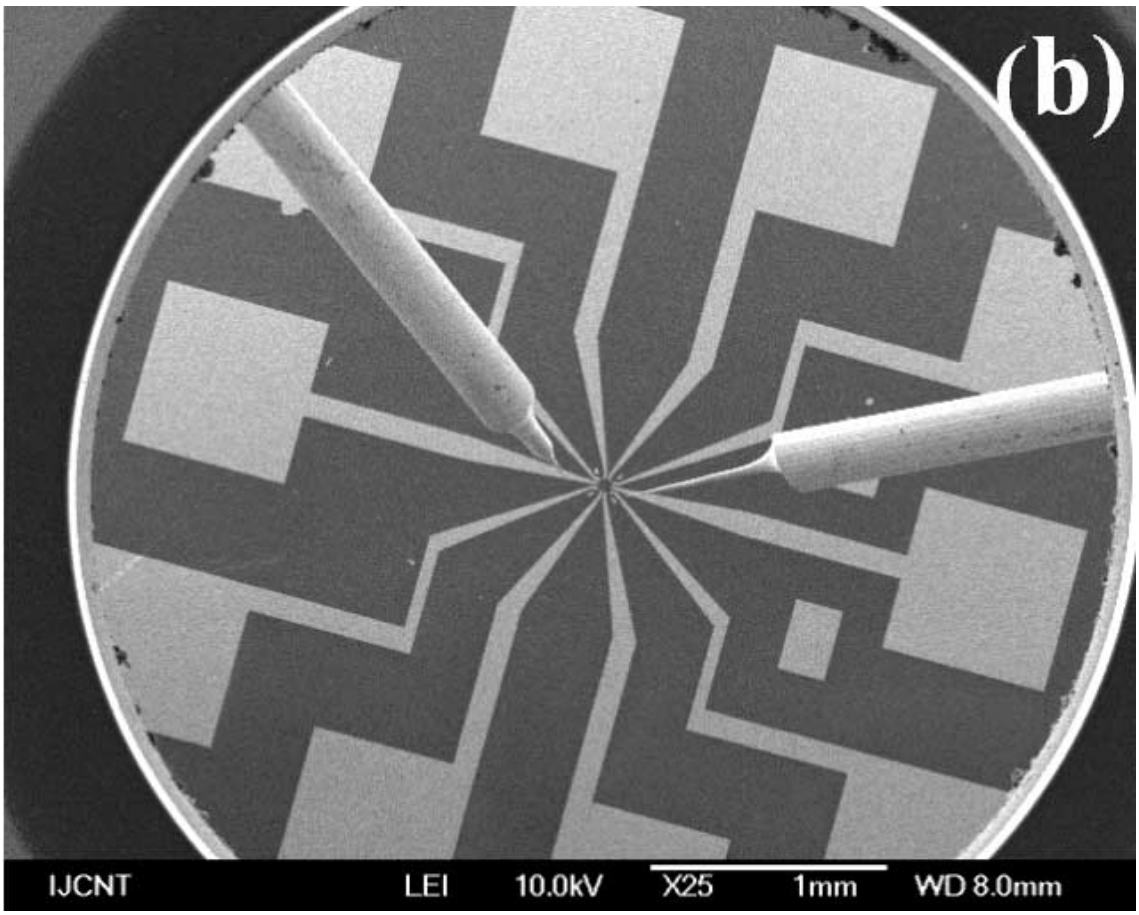

FIG. 1. (b) Electrochemically etched W tips attached at the end of the manipulators.

The etching parameters for W tip have been described elsewhere.[14] Another advantage of this approach is that the combination of FE-SEM and two manipulators allows us also *in situ* characterization.

The multiwalled carbon nanotubes (MWCNTs) generated by non-catalytic arc discharge were used for the test of our manipulators. During the CNT synthesis, the chamber pressure was maintained at about 360 torr with He gas. The diameter of the tubes ranges from 30 to 50 nm and the tube is metal-particle free. A fragment of soot was brought into a specimen chamber. Fragments usually revealed nanotubes sticking out in all directions, as shown in the left in Fig. 2(a).

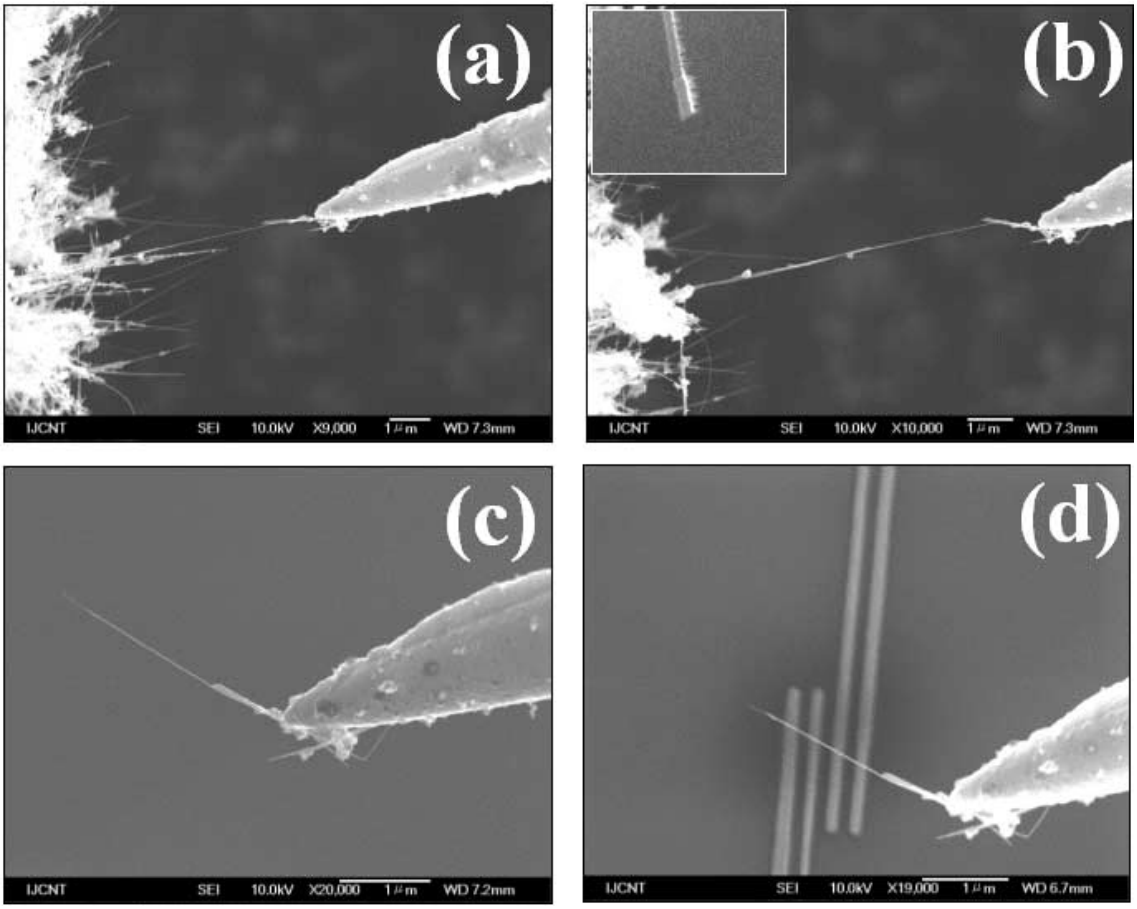

FIG. 2. Panoramic images of fabricating carbon nanotube transistor on pre-patterned electrodes on a Si substrate. The inset shows the deposition of hydrocarbon at the end of a MWCNT under e-beam irradiation; (a) adhesion of a bundle at the end of W tip; (b) separation of a bundle from the fragment of the soot; (c) a strand of MWCNT adhered on the bundle; (d) approach of the MWCNT to the substrate;

We carefully moved one of manipulators until the tungsten tip touched a bundle of the MWCNTs on the fragment. We then focused the electron beam on the contact area between the bundle and W tip and intensively irradiated for around 10 minutes in order to solidify the adhesion. The acceleration voltage and beam current were 10-15 kV and 10 μA, respectively. This procedure was very necessary to adhere the bundle to the W tip, as shown in the right in Fig. 2(a).

We next demonstrate how to attach another carbon nanotube to the bundle. Once we make sure that the bundle is in touch with the single strand of the nanotube, as shown in Fig. 2(b), we again focused our electron beam to the contact area to enhance adhesion. The adhesion is achieved by depositing an extra material in the contact, where the inset demonstrates one end of nanotube exposed to the electron beam to be swollen. This electron beam-induced deposit (EBID) is reportedly attributed to the hydrocarbons.[15] The deposition rate depends on the chamber pressure, beam current, sticking coefficient, and sample purity.[16] We note that a measurable size of the deposit is required for the secure adhesion. Once we make sure that the tube was attached, we pulled out the nanotube by moving the manipulator away from the fragment of nanotubes. A single strand of the MWCNT was separated from the bundle, as shown in Fig. 2(c). We tried another way to adhere the nanotube to the W tip.[17]

We now demonstrate how to construct carbon-nanotube transistor prepared on the patterned electrodes, where four electrodes are aligned in parallel within a μm. In order to place an individual MWCNT on those electrodes, we first moved a single strand of nanotube onto the electrodes, as shown in Fig. 2(d). A new CNT bundle on W tip of another manipulator was prepared by similar EBID method. The purpose of using a new bundle is to protect the metal electrodes on substrate, since W tip can easily damage the electrode as it accidentally strikes the electrodes during manipulation. Furthermore, this nanotube bundle provides a better flexibility and higher aspect ratio to W tip, which is advantageous for nanomanipulation. This enabled us to press a single strand of nanotube placed already on the electrode without damage, as shown in Fig. 2(e).

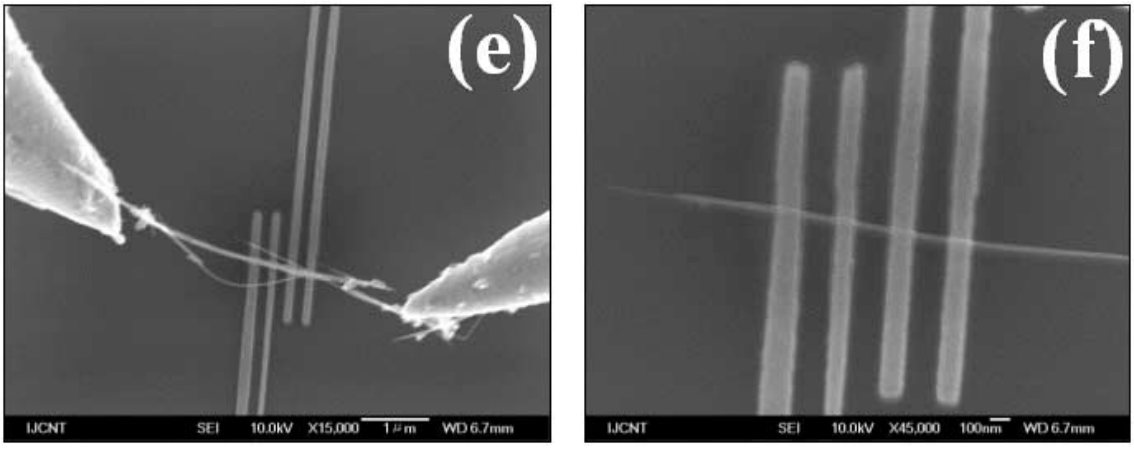

FIG. 2. Panoramic images of fabricating carbon nanotube transistor on pre-patterned electrodes on a Si substrate: (e) positioning the MWCNT on electrodes and pressing the MWCNT by the counter CNT bundle; and (f) fabricated carbon-nanotube transistor.

The other manipulator was then pulled out carefully, which left a single strand of the nanotube successfully on the metal electrodes, as shown in Fig. 2(f). We emphasize that our approach with two maneuverable manipulators can save labor time and reduce the trial and error during the manipulation and could be applied for any type of

interconnections between nanostructured materials and macroworld characterization systems and even in cautious MEMs fabrications.

In addition to positioning a nanotube on electrodes, we also attached a MWCNT at an AFM tip with a blunt apex, as shown in Fig. 3(a). During the operation, we often observed that an electrostatic force exerted between the nanotube and AFM tip, which may be caused by the different amount of charges accumulated on the nanotube and AFM tip. This force attracted the nanotube towards the AFM tip and the nanotube abruptly stuck to the tip. When the nanotube was misaligned to the tip axis, we carefully dragged the nanotube to align along the tip axis by the counter manipulator. Several areas on the AFM tip were locally spot-welded with the EBID. Since the nanotube was well adhered at the tip, we separated the counter manipulator by snapping it from the nanotube at the AFM tip. Figure 3(a) clearly shows that an individual MWCNT is protruded sharply along the AFM tip.

One of the interesting properties observed during manipulation with MWCNT is an elongation of the nanotube. This was observed, when both W tips connecting a single strand of the MWCNT were pulled out from each other. Figure 3(b) shows the extraction of the nanotube with the thinner tube at the elongated part. This is called sword-in-sheath effect.[18] The thinned tube is kinked because of the non-orthogonal movements of our nanomanipulator. We conjecture that the inner tube was pulled out as the outer tube was broken apart due to the tensile force, since only the outer tube was bound to the W tip by hydrocarbon deposit. The sliding motion of the outer wall is known to be frictionless.[19]

It is observed that the hydrocarbon deposit is very simple and convenient means for welding nanostructured materials. A strong adhesion between the nanotube and W tip was established through this method. It is physically strong enough to endure the tensile stress that breaks apart the MWCNT wall. The electrical conductivity of the junction could be also an important issue. Therefore, we measured the conductivity of the junction by connecting two manipulators through a single strand of the MWCNT, as shown in Fig. 3(c).

The I-V curve is demonstrated in Fig. 3(d) and the characteristics of the I-V curve is under study.

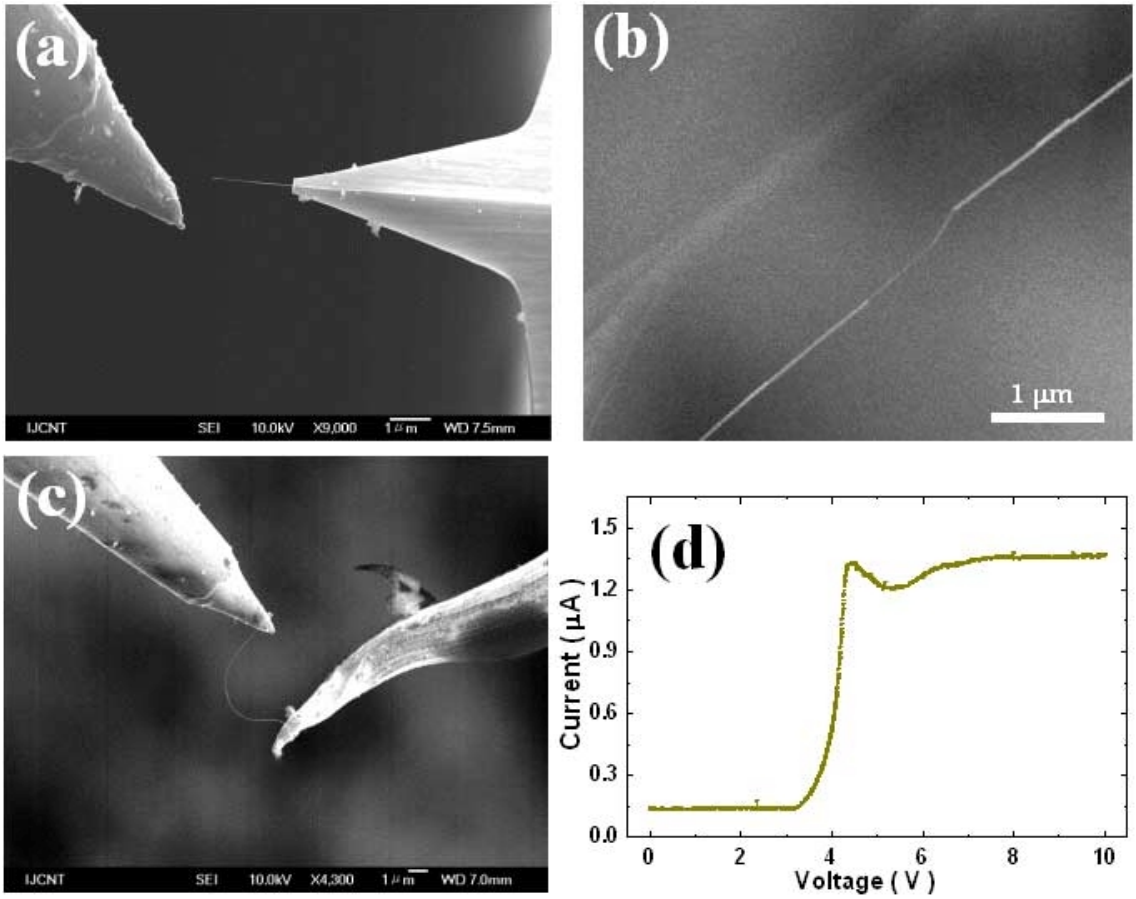

FIG. 3. (a) Attachment of a MWCNT at the AFM tip. (b) The elongation of a nanotube with the fracture of the outer layer. (c) Intentional bending of the MWCNT by squeezing two manipulators. (d) The I-V curve measured from Fig. 3(c).

The deposit at the junction is an amorphous material composed of oxygen, hydrogen, and carbon with a moderate conductivity that allows a tunneling current in scanning tunneling spectroscopy (STS).[20,21] Our results, however, indicate that the deposition of hydrocarbon resulted in extremely high resistance. It is possible that the oxidation layer on the W tip might be attributed for such a high resistance. However, we simply ruled out this possibility, since the head-on contact between two W tips reduced the resistance down to a few ohms. We presume that the constituting oxygen atoms in the deposit with carbon might form the oxygen-related functional groups such as carboxylic and hydroxyl groups, resulting in poor electrical conductivity. Removal and transformation of these groups into amorphous and graphitic carbon, which will create conducting paths, require high temperature annealing or irradiation of energetic ion beam.[21,22]

In summary, we have demonstrated successfully various manipulations of CNTs inside FE-SEM. The integration of FE-SEM and two manipulations enables us to do *in situ* manipulations and characterizations. Our system with two nanomanipulators also allows more degrees of freedom, which lead to the diversity in operation. We observe that the EBID method is useful to weld CNT junctions mechanically onto the W tip and invokes highly resistive junctions. A new approach with good conductivity in

naonoscale is to be developed.

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[17] Another alternative to adhere the nanotube to the W tip is to apply a bias voltage between the tip and the MWCNT after positioning the W tip close to the nanotube. The nanotube can be adhered to the tip with a sudden increase of current at around a few hundred volts. However, the nanotube disappears sometimes due to an excessive current. Another disadvantage of this approach is the poor reliability initiated by the complicated geometry of abundant adjacent nanotubes near the junction. These adjacent nanotubes sometimes lead to unpredictable adhesion by defocusing the electric field between the nanotube and the tip.

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