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Letters to the Editor

Fabrication of multilayered nanotube probe tips

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Since its discovery [1] in 1991, carbon nanotubes (CNT) have attracted intense attention because of their potential applications [2–9] in advanced technologies. Different synthesis techniques have been developed, for example: (1) the carbon arc discharge method [1,10], (2) laser ablation [11] of graphite, and (3) catalytic vapor growth [12]. Most of these techniques involve only relatively simple and inexpensive equipment. It is fairly routine now to produce CNTs in small quantities in a research laboratory. However, the study of physical properties of individual CNT required much more sophisticated instrumentation due to the nanometer size of CNTs. The obstacle of handling CNT without an electron/scanning probe microscope has posed a formidable challenge and has hampered both current research and future applications of CNTs.

One of the potential applications of carbon nanotubes is as tips for scanning probe microscope. As microelectronics fabrication continues to shrink, there is a great need [13] to qualify the high-aspect-ratio features. Dai et al. [14] recently has demonstrated that a carbon nanotube bundle glued to the pyramid tip of a conventional scanning probe microscope can be used to image 400 nm wide and 800 nm deep trenches in silicon. However, the task of attaching nanometer size CNT bundle under direct view of an optical microscope is quite challenging to say the least. More recently, Cheung et al. [15] has developed a catalytic CVD surface growth method to grow single wall and multi-wall carbon nanotubes directly on the silicon tips of atomic force microscopes. In the following, we report a processing technique for the fabrication of carbon nanoprobes, which can be used in AFM.

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The growth technique we adopted was based on the catalytic vapor growth [12] of CNTs. Catalysts of 50:50 Fe/Ni alloy nanoparticles were first deposited [16] on a silicon substrate under 5 Torr of Ar atmosphere from a tungsten evaporation boat. The typical size of the nanoparticles deposited were 5–20 nm in diameter. The coated Si substrate was then put inside a tube furnace. A methane, hydrogen, and argon mixture was flown through the furnace at elevated temperature under one atmosphere pressure. Between 725 and 1050 °C, carbon fibers and CNTs can be grown [17]. Below 850 °C, the only observed deposition appeared to be associated with catalytic processes. At about 875–900 °C, the onset of non-catalytic thermal decomposition of methane began, with traces of non-fibrous graphitic material beginning to form on the reactor wall. Deposition of non-catalytically decomposed graphitic material increased with increasing temperature, but only becomes troublesome at temperatures above 1000 °C. Dilution of methane with argon or an argon–hydrogen mixture lessens the problems associated with non-catalytic deposition. We found that at lower temperatures, when only the catalytic growth mode is operative, the size of the carbon nanotubes is mainly controlled by the size of the nano-catalysts. When the temperature is above 875 °C and pressure at 1 atm, spontaneous decomposition of methane starts to occur. Under such condition, amorphous carbon starts to deposit on the outside wall of the nanotube and thicken the diameter of the carbon nanotube.

Our main goal in this research is to develop a method for the growth of a configuration of carbon nanotube that would be easy to handle and at the same time can be used for AFM tip and electron field emission applications. Our approach is to grow a 10–30 nm diameter carbon nanotube core with an outer graphitic layer about 1 μm in diameter. The whole assembly of carbon fiber/nanotube is visible

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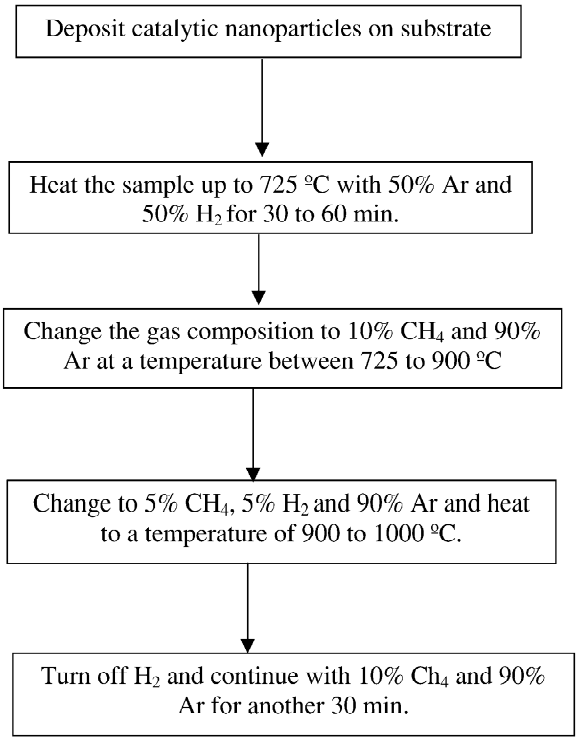

Fig. 1. CVD process steps for carbon nanotube probe tips.

under conventional optical microscope and can be manipulated by optical means. We adopt the following strategy to accomplish the task. We first heat our substrate under a 50:50 mixture of Ar and H_2 to 725 °C to purge the growth chamber and to reduce the nanoparticles to metallic form. Then we turn off H_2, add 10% methane with Ar, and continue heating the substrate to 875 °C. During this stage, carbon nanotubes are grown on the silicon substrate by the catalytic vapor growth process. The length of the nanotube depends on the growth duration while the diameter of the nanotube is mainly controlled by the initial catalyst particle size. We then reduce the methane concentration to 5% of the total mixture and add 5% H_2 and anneal the nanotube between 900 and 1000 °C for a fixed duration. This step is necessary to deposit a thin layer of amorphous carbon on the outside wall of the CNTs. Afterward, we increase the methane concentration to 10%, turn off the supply of H_2, and heat the sample at 1000 °C for another fixed duration. During this final step, a graphitic carbon outer layer is deposited on top of the amorphous carbon. In Fig. 1, a flow chart of our multi-step vapor growth processing conditions for the growth of the carbon nanoprobe is shown.

After chemical vapor deposition, the carbon fibers are broken down mechanically with a razor blade. Since the mechanical strength of carbon nanotube is much greater than that of the graphitic carbon, it is possible to break the graphitic carbon loose without breaking the carbon nanotubes. The broken carbon fibers are then examined using a JEOL 6400 scanning electron microscope. The carbon fibers are clearly shown in Fig. 2a. The typical diameter of the carbon fibers is about 0.1–1 μm, and typical length is about 50–500 μm. We choose the conditions where the fibers are not too densely nucleated for ease of handling. In Fig. 2b, a carbon fiber is broken to reveal the inner nanotube core. It can be seen that the diameter of the nanotube inside the carbon fiber is about 20 nm and about 1 μm of the nanotube extends past the graphitic shell.

The multi-step process we described above is important for generating this particular structure of a carbon nanotube embedded in a carbon fiber. We note that the

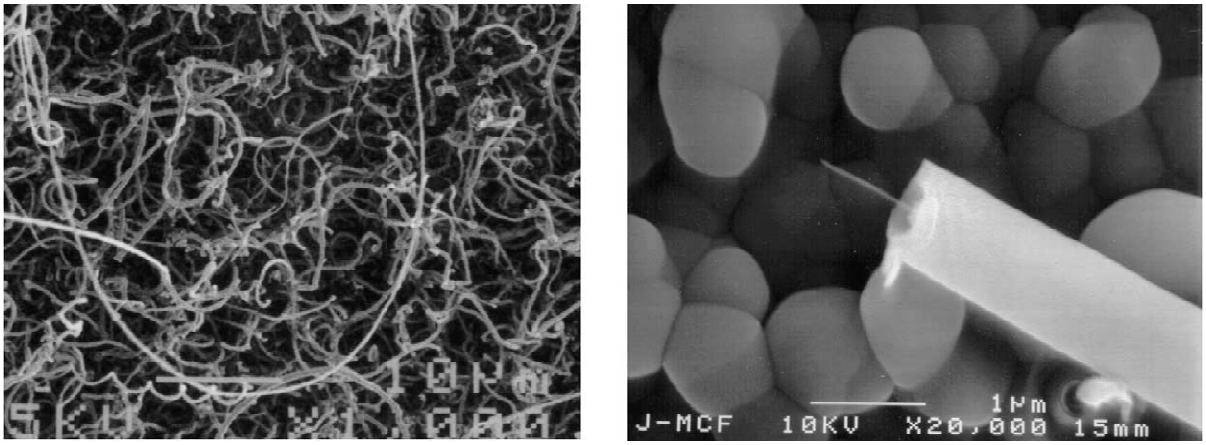

Fig. 2. (a) SEM micrograph of carbon nanoprobes grown under the conditions listed in Fig. 1. The diameter of the outer graphitic layer is about 1.2 μm. (b) This carbon nanoprobe has it outer graphitic layer partially broken. The nanotube core is extended out about 1 μm from the end of the carbon fiber.

growth of an intermediate layer of amorphous carbon between the nanotube and the graphitic carbon fiber is very important. Without the interfacial amorphous carbon layer, the strong bonding between the nanotube and the outer graphitic layer tends to make the whole assembly break at the same point, resulting in a smooth surface without the nanotube sticking out from the end. To verify that the central core of the carbon fiber is indeed composed of carbon nanotube as we expected, we examined the carbon fiber using a high resolution scanning transmission electron microscope (Tecnai F30, TEM/STEM). From the images in Fig. 3a and b, it is clearly shown that the inner core is a MWNT with a diameter of 22 nm, while the outer layer is consists of graphitic carbon.

There are two advantages of this configuration of carbon nanoprobe. The first is the fact that the size of the outer graphitic fiber is about 1 μm or more so the nanoprobe assembly can be handled with an optical manipulator. Secondly the nanotube is protected by a much larger graphitic fiber which is usually straight for a length of ten to twenty ìm. To demonstrate the usefulness of this new configuration, we use a Focused Ion Beam (FEI TEM 200) to fabricate a trough on the edge of a silicon substrate. We then mounted the carbon nanoprobe inside the trough and used the deposition mode of FIB to deposit a Pt metal strip to weld the carbon nanoprobe onto the silicon substrate (Fig. 4). This configuration can be easily adapted to the AFM tip application or the electron field emission application.

Carbon nanotubes are potentially useful as mechanical, electrical, and chemical probes. The principal difficulty associated with their application lies in finding an efficient method for handling these materials which are of nanometer dimensions. The process demonstrated here offers a possible solution. This technique permits the fabrication of carbon nanotubes with a macroscopic 'handle' thus permitting the use of conventional optical manipulators. In addition, the length of the carbon fiber with nanotube core are often several tens or hundreds of micrometers. It then becomes possible to fabricate multiple probe tips, each has the same length, and sharing virtually identical other physical properties.

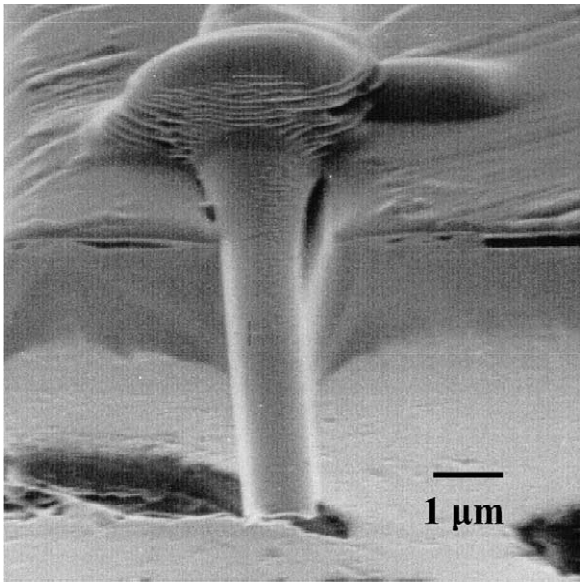

Fig. 4. A carbon fiber mounted in an FIB fabricated trough in silicon and welded with FIB deposited Pt metal.

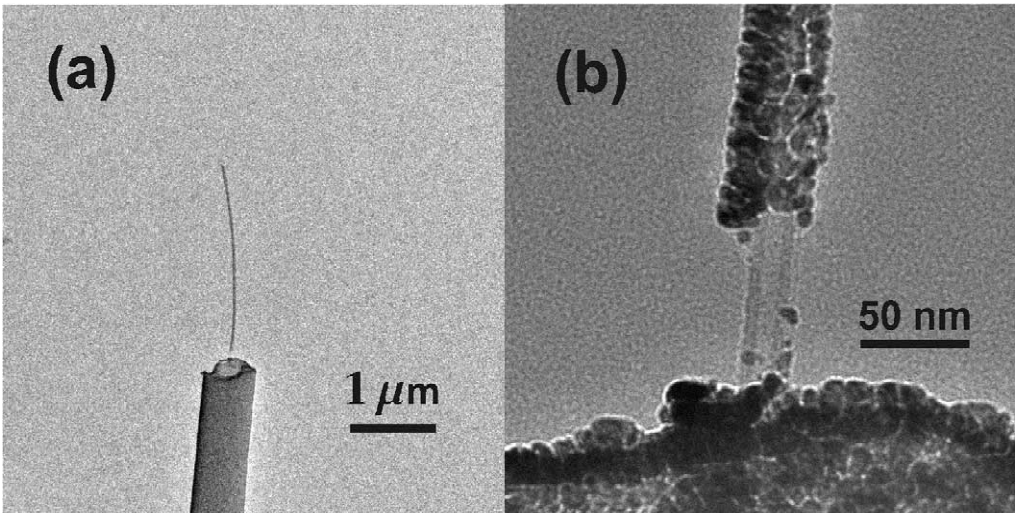

Fig. 3. (a) TEM image of a single carbon fiber that contain a nanotube as its core. (b) High resolution image of (a) showing the carbon nanotube. Note the sample was coated with a layer of Au/Pd alloy before imaging in an SEM. This coating is seen covering part of the nanotube and the graphitic shell.

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Chemical vapor deposition of carbon films: in-situ plasma diagnostics

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Chemical vapor deposition (CVD) is conventionally used to create a variety of carbon mesomaterials including polycrystalline diamond films [1] and carbon nanotubes (CNT) [2]. The remarkable flexibility of the CVD process

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