Carbon Nanotube Growth for GHz Devices

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***Abstract*— Horizontally oriented single walled carbon nanotubes are grown with CVD between lithographically defined catalyst sites. Single walled carbon nanotubes up to 60 μm in length are grown using methane as the feedstock. The nanoparticle catalyst is deposited from a newly developed aqueous solution requiring only photoresist and optical lithography. Carbon nanotube Y-junctions are also observed and characterized.**

I. Introduction

In this paper we describe the growth of carbon nanotubes for the development of GHz electronic devices. Recently one of us[1], [2] predicted that the inductance of a nanotube should be very large ($\sim$10 nH/μm) based on the kinetic inductance inherent in any 1d quantum system. However, in order to measure that kinetic inductance electrical contact to the nanotube is required. Rather than using dc ("ohmic") contact, we proposed to use a capacitive contact. A capacitive contact is in principle simple to achieve: any parallel plate close to the nanotube will be capacitively coupled to the nanotube. At GHz frequencies, this capacitance can behave as a short circuit, allowing efficient (i.e. low-impedance) high-frequency contact to a nanotube. However, for this to be the case, the length of the nanotube must be significant, even for parallel plates very close to the nanotube.

Further reflection reveals that a capacitively contacted nanotube has a distributed capacitance per unit length as well as a distributed kinetic inductance per unit length, thus forming an electrical transmission line. (This is a circuit description of the fundamental excitations in a Lüttinger liquid.) We further predicted that it would be possible to measure the wave velocity of this nano-transmission line by measuring the GHz electrical impedance from plate-to-plate, as shown in figure 1. For GHz resonant frequencies, nanotubes of order 100 μm in length must be grown.

In this paper we present growth of nanotubes long enough to behave as electrical nano-resonators with resonant frequencies in the GHz range. Our nanotubes are grown using CVD. Our catalyst preparation is similar to that of Kong[3] but can be deposited using a lift-off procedure requiring only photolithography and standard photoresist, in contrast to that of Kong which required either electron beam lithography or UV lithography on PMMA.

Our catalysts have allowed the growth of many Y-junction nanotubes, which we describe and analyze quantitatively.

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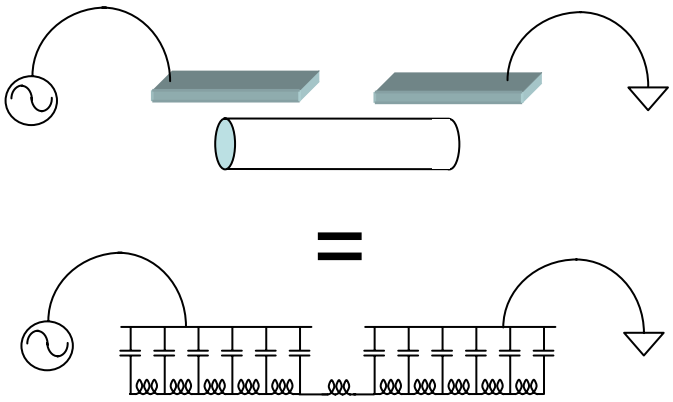

Fig. 1. Predicted effective circuit model for capacitively contacted nanotube.

II. Catalyst Preparation

Under methods developed in reference [3], alumina nanoparticles combined with transition metals are typically mixed in methanol and spun onto a wafer with pre-patterned PMMA wells. This requires either 1) electron beam or deep-UV lithography to pattern the PMMA directly, or 2) a multi-step process involving both PMMA and photoresist. (Methanol cannot be spun onto wells patterned into photoresist directly because it dissolves the photoresist.) We have developed a simplified method of depositing transition metal catalysts using an aqueous solvent for the nanoparticles and transition metal catalysts.

Using conventional photolithography we fabricate wells directly in photoresist (Shipley 1827) on a 4" silicon wafer (100, p-type, resistivity 12-16 kΩ-cm) with its native oxide. Next, 2.0 g of alumina nanoparticles (Degussa, aluminum oxide C), 2.5 mmol of $Fe(NO_3)_3 \bullet 9H_2O$ (Aldrich), and 0.7 mmol of $MoO_2(acac)_2$ (Aldrich) are added to 60 ml DI water in sequence while violently stirring. Since the $Fe(NO_3)_3$ is

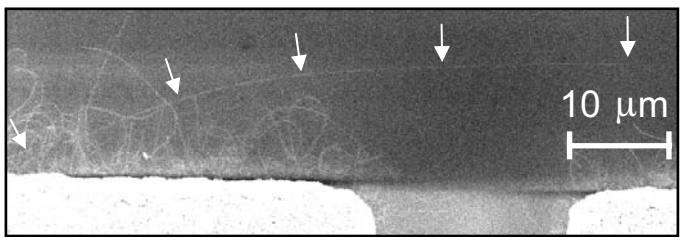

Fig. 2. SEM image of a single walled carbon nanotube. Length is 60 μm.

soluble in water, spinning this solution directly onto the wafer would remove most of the Fe. This would be an undesirable consequence, essentially throwing out the baby with the bath water, since the Fe plays a crucial catalytic role in the nanotube growth. To alleviate this problem, 15 ml of ammonia (concentrate) was slowly dropped into the mixture above. This caused the formation of $Fe(OH)_3$, which precipitates:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (1)$$

$$Fe^{3+} + 3\ OH^- \rightarrow Fe(OH)_3 \downarrow \quad (2)$$

The mixture was stirred for 24 hours followed by sonication for 3 hours, resulting in a suspension of 1.25 mmol Fe_2O_3/0.7 mmol MoO_3/2.0 g alumina and water. Two drops of this suspension were deposited onto the patterned photoresist. After spinning on the suspension at 3400 rpm for 40 seconds, and after a 100°C 20 minute bake, lift-off of the photoresist in acetone led to the final sample with catalyst pattern ready to carry out CVD.

In contrast to reference[3], we did not achieve high uniformity of the catalyst thickness. This is probably because the concentration of nanoparticles used was approximately 100 times higher than that of reference[3]; future work will use lower concentrations.

III. Growth Procedure

CVD was carried out using a 3" Lindberg furnace. A gas recipe that favors the synthesis of ultra-long and high quality SWNTs was adopted in the experiment. After heating up the 3" quartz tube to 900°C under an argon atmosphere, the argon was replaced by a co-flow of 1000 sccm methane (99.999%), and 200 sccm hydrogen for 12 minutes. All the process were performed under manual control, including purging Ar, increasing the temperature, flowing active gases and cooling down the system in the Ar atmosphere again. Significant scalability is possible with our CVD system since the active region in the furnace was found to be more than 2" x 5" as long as the appropriate temperature can be maintained.

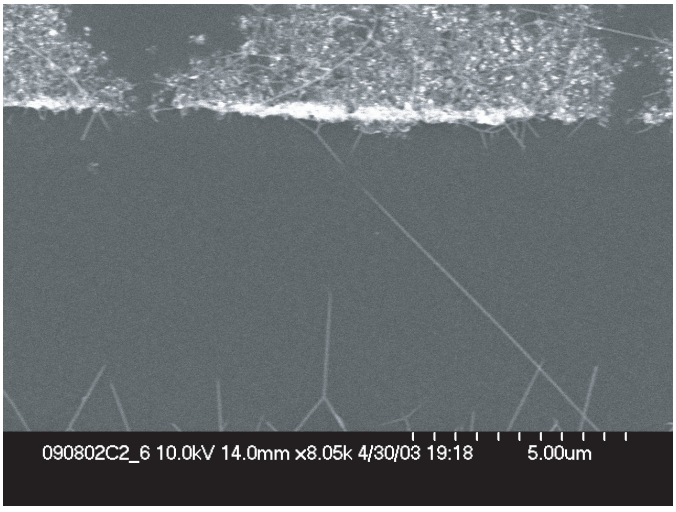

Fig. 3. SEM images of Y-junction.

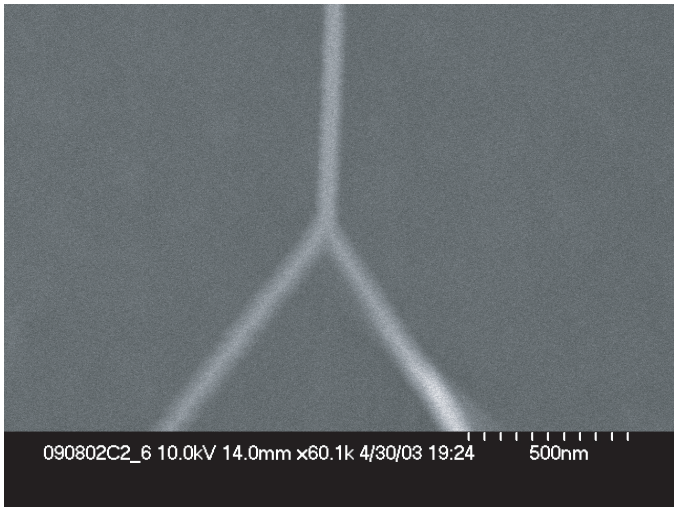

Fig. 4. High resolution SEM image of Y-junction.

IV. Growth Results

As-obtained samples were characterized by a scanning electron microscope (SEM) (Hitachi S-4700) using beam energies of 10-15 keV.

The nanoparticle catalysts produced nanotubes in abundance where the catalyst was uniform. AFM images of growth results from a similar experiment (Shengdong Li, *et al*, unpublished) show that the diameter of as grown nanotubes is less than 1.5 nm, which agrees well with the literature[3] using this technique with nanoparticle catalysts. Thus we infer that the nanotubes grown from the nanoparticle catalysts are single walled. An SEM image of a typical growth result is shown in figure 2. One can clearly see that a single walled carbon nanotube of length 60 μm has been grown.

The gas recipe described above is essential for the success of this experiment. First of all, rather than using less stable acetylene known to produce MWNTs at 700-800 °C as the carbon source, high purity methane was used to favor the production of SWNTs. H_2 was used to suppress the deposition of amorphous carbon and thus maintain the high purity of as obtained SWNTs.

V. Y junctions

Investigation under SEM also revealed several Y-junctions A typical Y-junction is shown in figures 3,4. We expect that the Y-junction is actually an individual nanotube. AFM characterization is currently underway to verify this conclusion. We show in figure 5 a histogram of the number of junctions vs. angle subtended. Our work indicates an increased occurence at a set of three discrete angles. These may be correlated with the chemical nature of the carbon-carbon bond and how it influences the angles of Y-junctions. Previous work on Y-junctions includes for example references [4], [5].

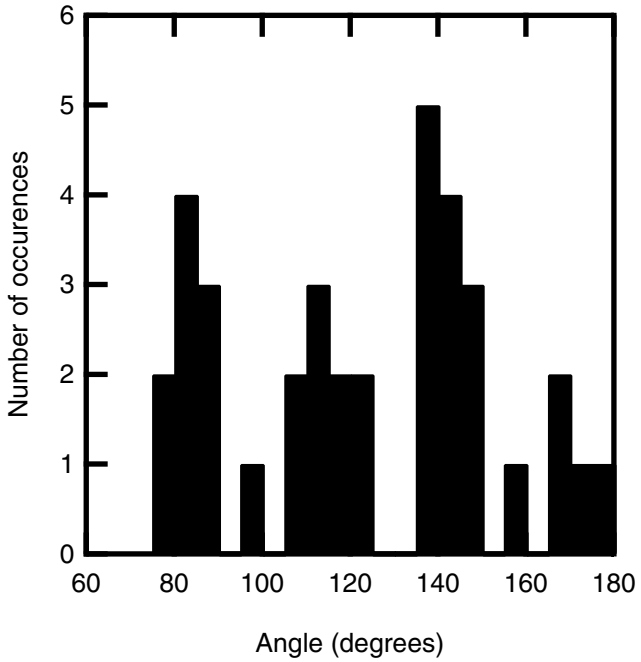

Fig. 5. Histogram of number of angles observed.

VI. Conclusions

We have presented growth results using nanoparticle catalysts dispersed in aqueous solvent. Nanotubes as long as 60 μm have been grown. Further fabrication and processing development is underway to measure the GHz impedance of capacitively contacted nanotubes. Our work on the GHz electrical properties of nanotubes described so far has been for passive resonator devices. However, the models developed lay the intellectual foundation for understanding *active* nanotube devices, ultimately answering the question: What is the speed limit of molecular electronics?

Acknowledgments

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