

# High-throughput top-down and bottom-up processes for forming single-nanotube based architectures for 3D electronics

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## ABSTRACT

We have developed manufacturable approaches to form single, vertically aligned carbon nanotubes, where the tubes are centered precisely, and placed within a few hundred nm of 1-1.5  $\mu\text{m}$  deep trenches. These wafer-scale approaches were enabled by chemically amplified resists and inductively coupled Cryo-etchers for forming the 3D nanoscale architectures. The tube growth was performed using dc plasma-enhanced chemical vapor deposition (PECVD), and the materials used for the pre-fabricated 3D architectures were chemically and structurally compatible with the high temperature (700 °C) PECVD synthesis of our tubes, in an ammonia and acetylene ambient. Tube characteristics were also engineered to some extent, by adjusting growth parameters, such as Ni catalyst thickness, pressure and plasma power during growth. Such scalable, high throughput top-down fabrication techniques, combined with bottom-up tube synthesis, should accelerate the development of PECVD tubes for applications such as interconnects, nano-electromechanical (NEMS), sensors or 3D electronics in general.

## INTRODUCTION

The constant drive toward miniaturization driven primarily by the microelectronics industry has created niche opportunities for nanoscale materials, such as carbon nanotubes that show promise as interconnects,<sup>1</sup> novel transistors,<sup>2</sup> or heat transport materials.<sup>3</sup> A heavily utilized technique for the synthesis of carbon nanotubes, specifically multi-walled-nanotubes (MWNTs), is thermal chemical vapor deposition (CVD), which results in ‘bundles’ of tubes largely perpendicular to the substrate. Inspection of MWNTs in such bundles reveals individual tubes growing in random directions and forming a ‘matted’ array.

A technique which has emerged in recent years to ensure excellent vertical tube alignment is plasma-enhanced (PE)-CVD,<sup>4</sup> where the inherent E-field in the plasma allows tube growth in a direction parallel to the field. Analysis of crystallinity of individual tubes reveals graphitic structures where the graphene layers are inclined to the central axis,<sup>5</sup> structures commonly referred to as carbon nanofibers (CNFs); however, control over their physical orientation with the plasma is excellent.

Besides the ability to direct growth orientation, another important figure of merit for many applications is the precise control over tube placement. There have been many reports on the PECVD growth of multiple tubes formed at controlled locations using positive tone novalac/diazoquinone-based or negative tone rubber/azide resists. When only single tubes are desired where the catalyst size has to be controlled below a few hundred nm, such resist systems

show excessive absorption in the deep-UV region, and are inadequate for deep-submicron feature size resolution. To date, e-beam lithography has been the main technique implemented for catalyst definition for the realization of arrays of individual, free-standing, vertically aligned CNTs or CNFs using PECVD.<sup>6</sup> However, e-beam lithography is slow and expensive, and ultimately limits the transition of nanoscale devices from the laboratory into commercial production. Moreover, in reports to date, single, vertically aligned tubes formed with PECVD have typically been grown on planar 2D substrates. In this paper, we describe approaches to form single, vertically aligned tubes in 3D nanoscale architectures using high throughput nanomanufacturable techniques. Such approaches should accelerate development of PECVD grown tubes for a broad range of applications, such as nano-electro-mechanical-systems (NEMS), interconnects, sensors, and 3D electronics in general.

## **EXPERIMENTAL DETAILS**

A schematic of our load-lock based PECVD growth chamber is provided elsewhere.<sup>7</sup> The starting substrate was typically a degenerately doped Si wafer (1 - 5 m $\Omega$ -cm) with pre-patterned features on it. After Ni catalyst deposition, a pretreatment step was typically carried out for 1-2 min. prior to CNT growth, where a low power hydrogen plasma (60 W, 5 Torr) reduced the surface oxide on the Ni at 700 °C. Following pretreatment, the chamber was pumped out until the pressure was restored to  $\sim 2 \times 10^{-6}$  Torr, after which point high purity acetylene (C<sub>2</sub>H<sub>2</sub>) and ammonia (NH<sub>3</sub>) were introduced, which served as the carbon feedstock and diluent gas, respectively. When the desired growth pressure had been attained, the dc discharge was ignited, and growth was carried out for a fixed duration. After completion, the samples were immediately transferred into the load lock for cooling and imaged using the SEM (JEOL-6700F).

## **DISCUSSION**

### **Top-Down Nanofabrication**

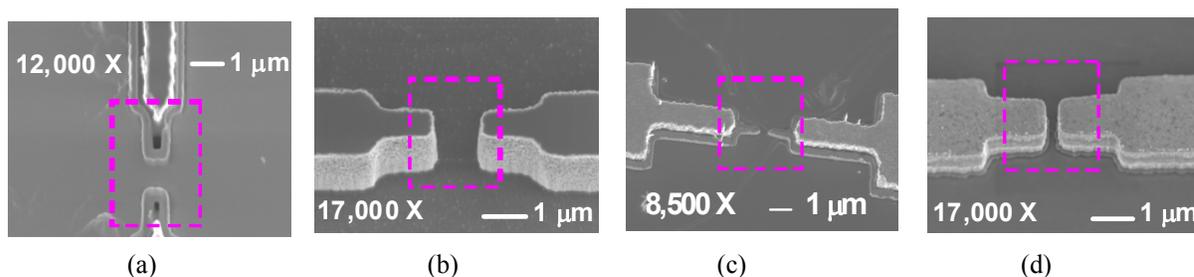
The position selective growth of CNTs is important for applications where tube growth is desired at only certain locations. Positive tone novalac/diazoquinone-based or negative tone rubber/azide-based resists have been used to form multiple tubes with PECVD at selected locations. In order to form single tubes, it has been determined that a catalyst diameter below about 300 – 400 nm is necessary.<sup>6</sup> E-beam lithography has typically been used to define the catalyst film when single tubes are desired, but this technique is limited by low processing speed and high cost, posing a severe impediment to applications and manufacturability.

We initiated the growth of single, vertically aligned tubes using dc PECVD, where a deep UV ( $\lambda = 248$  nm) eximer laser lithography tool (Canon FPA-3000 EX3 stepper) was used in conjunction with chemically amplified polyhydroxystyrene resin-based deep UV resists to pattern Ni catalyst dots in the few hundred nm diameter range.

A variety of applications can emerge in 3D electronics, when isolated PECVD grown tubes can be integrated with 3D nanoscale architectures, such as electrodes that are within a few hundred nm of the tubes. We describe approaches that utilize high throughput, top-down nanomanufacturable techniques to form high aspect ratio 3D nanoscale architectures that are integrated with single, vertically aligned PECVD grown tubes.

The electrodes consisted of bilayer stacks of either degenerately doped  $\sim 1.0 \mu\text{m}$  thick Si Device layer, over a  $0.5 \mu\text{m}$  Burried-Oxide (BOX) layer on Silicon-On-Insulator (SOI), or a deposited Nb film on thermal  $\text{SiO}_2$  ( $0.8 \mu\text{m}/0.4 \mu\text{m}$ ). The stack, with an electrode width of  $\sim 0.4 \mu\text{m} - 1.0 \mu\text{m}$ , was to be etched  $1 - 1.5 \mu\text{m}$  down to the degenerately doped Si substrate, where tube growth was to be initiated using dc PECVD. A positive tone, chemically amplified resist, AZ 8250, was used to define the electrodes, but maintaining a vertical etch profile with minimal undercut of such high aspect ratio features required substantial optimization of etch chemistries.

Low pressure, high density plasmas have proven advantageous for defining small features precisely using the Deep-trench Reactive Ion Etching (DRIE) or the so-called BOSCH process.<sup>8</sup> In contrast, cryogenic etching, or Cryo-DRIE first proposed by Taichi<sup>9</sup> is becoming increasingly popular compared to the standard BOSCH process. In the BOSCH process, a fluorocarbon polymeric inhibitor layer is formed with  $\text{C}_4\text{F}_8$  plasma chemistry, for sidewall protection in order to fabricate high aspect ratio microstructures. In contrast, the Cryo-DRIE process utilizes a non-polymeric inhibitor layer for low-bias, fluorine ICP plasmas, which can be removed easily compared to a polymeric inhibitor layer. We implemented the Cryo-DRIE technique for the realization of our high aspect ratio electrodes.

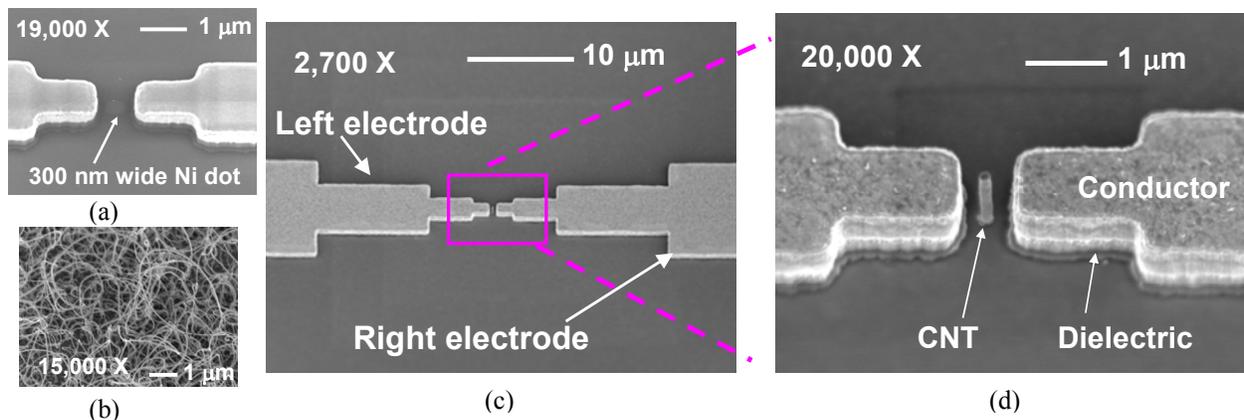


**Figure 1.** a) Si electrode etched in 100 %  $\text{SF}_6$  using a Fluorine ICP etcher, revealing severe undercutting of electrodes as viewed from the top. (b) Processes were developed to form high integrity Si electrodes using a combination of  $\text{SF}_6/\text{O}_2$  chemistries using Cryo-DRIE at 10 mTorr, 400 W ICP power, 100 W bias power, 80 sccm  $\text{SF}_6$  and 40 sccm  $\text{O}_2$ . Sidewall rippling was absent as is conventionally seen with the BOSCH process. (c) Similarly, Nb metal electrodes were severely distorted in an etch chemistry of  $\text{CCl}_2\text{F}_2/\text{CF}_4/\text{O}_2$ . (d) Chlorine ICP etch chemistries were optimized that resulted in minimal undercut of high aspect ratio, nano-scale structures, without compromising etch rates or selectivity (10 mTorr, 15 sccm  $\text{BCl}_3$ , 20 sccm  $\text{Cl}_2$ , 400 W ICP power, 100 W bias power). Tilt angle for (c) and (d) above was  $20^\circ$ .

The Si etching experiments were carried out in a Unaxis Fluorine ICP reactor (P-6857). In 100 %  $\text{SF}_6$  a severe undercutting of the Si electrodes was observed, as indicated by the SEM in Fig. 1a. The etch was optimized with the addition of  $\text{O}_2$  to  $\text{SF}_6$ , which formed highly anisotropy Si electrodes, shown in Fig. 1b. Moreover, unlike the BOSCH process operated in the time multiplexed mode, sidewall rippling was absent in Cryo-DRIE, since the sidewalls appeared smooth.

Similarly, we have experimented with etching thick metal films, such as Nb ( $\sim 0.8 \mu\text{m}$ ) using ICP etchers to control undercut. Again, severe pattern distortion was observed in a fluorine ICP etch chemistry, as shown by the electrodes in Fig. 1c. After optimizing etch chemistries, the SEM image in Fig. 1d depicts electrodes with smooth, vertical sidewalls and excellent structural integrity. With electrode etch chemistries optimized, the objective now was to control tube growth processes such that the tubes were centered precisely within electrodes such as Fig. 1d, by defining a Ni catalyst dot in the region between the electrodes.

The catalyst dot was defined using negative tone UVN 30 resist. After depositing Ni by lift-off, the sample was ready for CNT growth. Shown in Fig. 2a is the wafer after Ni lift-off, which reveals a 300 nm catalyst dot centered at the bottom of the 1.2  $\mu\text{m}$  trench ( $3\sigma$  overlay tolerance < 50 nm). Therefore, besides the ability to resolve few hundred nm features within deep trenches, the alignment accuracy of the Canon Stepper was extremely attractive for such multi-layer processes with stringent alignment requirements. The tube growth was then conducted using PECVD. Just for comparison, Figure 2b shows unoriented tubes that result without the presence of a plasma during CNT growth.

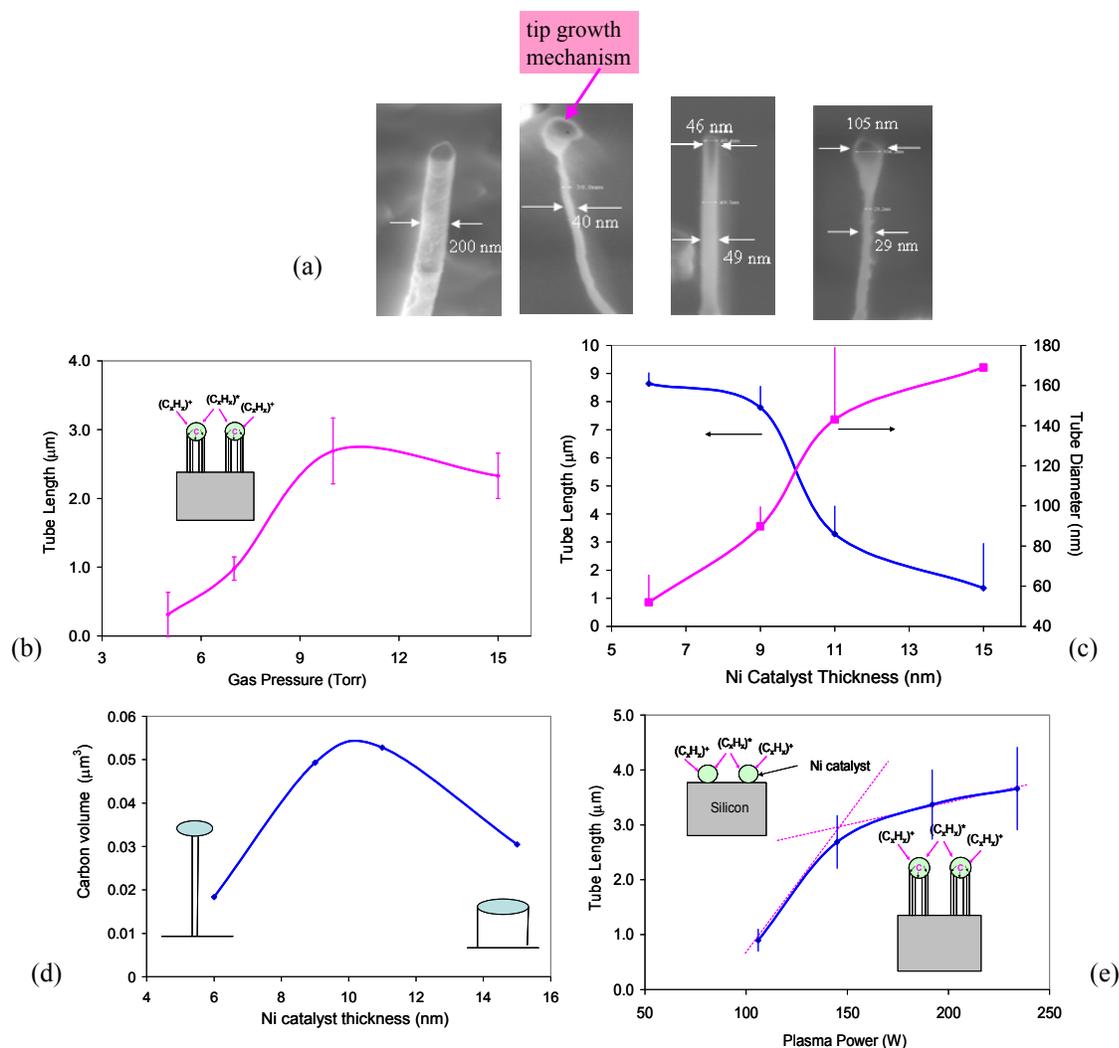


**Figure 2.** (a) Shown is a 300 nm Ni catalyst dot centered at the bottom of a 1.2  $\mu\text{m}$  deep trench. (b) Unaligned tubes result when  $\text{C}_2\text{H}_2$  and  $\text{NH}_3$  are used in the absence of an E-field during CNT growth. (c) The low magnification image shows electrodes on either side of a narrow gap, and (d) the high magnification image depicts a single, vertically aligned tube centered and < 300 nm away from the electrode that resulted from a typical catalyst dot, such as in (a). The processes developed here are amenable to high throughput nano-manufacturability, and incorporate both top-down fabrication and bottom-up synthesis.

In contrast, shown in Fig. 2c is a low magnification SEM image that depicts two Nb/SiO<sub>2</sub> electrodes. The high magnification image in Fig. 2d reveals a single, vertically aligned CNT that is centered, and within ~ 300 nm of ~ 1.2  $\mu\text{m}$  tall electrodes on either side. The high throughput approaches described here are completely amenable for the integration of PECVD grown tubes with 3D nanoscale architectures.

### **Bottom-up PECVD Tube Synthesis**

For the SEM images of Fig. 2d, the growth conditions used resulted in 200-250 nm wide tubes. For certain applications, tube characteristics may need to be engineered, such as the extent to which they emerge above the electrodes, or their diameters, which changes their mechanical properties. These characteristics were controlled to some extent, by adjusting the CVD growth parameters, such as growth pressure, catalyst thickness, and power. As an example, the SEM in Fig. 3a shows tubes of diameters ranging from 200 nm down to only 40 nm, which resulted from varying CNT growth parameters. Also, as is evident from this figure, a tip growth mechanism was operative, where the nominally pear-shaped<sup>10</sup> nickel cap, remains on the tip as the tube grows.



**Figure 3.** (a) Tube characteristics were engineered to some extent, via CNT growth parameters (pressure, catalyst thickness and power) and depict very wide  $\sim 200$  nm tubes down to tubes only  $\sim 29$  nm wide. A tip growth mechanism was also seen to be operative for Ni/Si. (b) Tube length as a function of pressure shows a near linear increase up to about 10 Torr, beyond which growth rate saturates. Conditions were 22 sccm  $C_2H_2$ , 90 sccm  $NH_3$ , 9 nm Ni thickness, 400 mA plasma current, and 6 min. growth time. (c) Tube length and diameter as a function of Ni catalyst thickness which suggests thin catalyst layers (e.g.  $\sim 5$  nm) nucleate narrow and long tubes, while thicker catalyst layers (e.g. 15 nm) nucleate short and wide tubes. Growth conditions were 22 sccm  $C_2H_2$ , 90 sccm  $NH_3$ , 230-240 W plasma power, 10 Torr, 15 min. growth time. (d) The dependence of tube volume (approximated as a cylinder) shows a maximal volume at about 10 nm in catalyst thickness. (e) Tube length as a function plasma power which indicates at a power below about 140 W, tube growth rate decreases significantly. Growth conditions were 22 sccm  $C_2H_2$ , 90 sccm  $NH_3$ , 10 Torr, 9 nm Ni thickness, 6 min. growth time. The data obtained above represents an averaging over 30 tubes.

A parametric investigation of the tube growth parameters (pressure, catalyst thickness and power) was also performed and the effect on the physical tube characteristics was analyzed. The results of this parametric variation are provided in Fig. 3b-(e); a more detailed discussion of these results is presented elsewhere.<sup>7</sup>

## CONCLUSIONS

In summary, we have developed a method for using high throughput, nanomanufacturable techniques for the realization of single, vertically aligned tubes integrated into 3D nano-scale architectures. Top down techniques, such as the use of deep UV chemically amplified resists for small feature size resolution, optical lithography units that allow unprecedented control over layer-to-layer registration, ICP etching techniques that result in near vertical, high aspect ratio 3D nano-scale architectures, in conjunction with the use of materials that are structurally and chemically compatible with the high temperature CVD synthesis of our PECVD grown tubes, were all key elements to the realization of these architectures. The wafer-scale techniques developed here should accelerate the integration of PECVD grown nanotubes for a wide variety of applications in electronics and sensing.

## ACKNOWLEDGMENTS

We thank Dr. Choonsup Lee for useful discussions and Dr. Henry LeDuc for the use of deposition equipment. This research was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration and was funded through the internal Research and Technology Development (R&TD) program.

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