Large-Scale Fabrication and Assembly of Carbon Nanotubes via Nanopelleting

by

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Submitted to the Department of Mechanical Engineering in Partial Fulfillment of the Requirements for the Degree of Master of Science at the Massachusetts Institute of Technology

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Abstract

Widespread use of carbon nanotubes is predicated on the development of robust large-scale manufacturing techniques. There remain, however, few feasible methods for the large-scale handling of aligned and geometrically uniform carbon nanotubes (CNTs), which has limited successful commercial applications to date. This thesis investigates a process, termed nanopelleting, for the handling and assembly of CNTs that allows integration into multi-scale systems with direct control over CNT length, alignment, and position over large areas.

Conceptually, a nanopellet consists of a CNT embedded within a micro-scale block. The block serves as a micro-scale transport vehicle, or carrier, for the nanostructure, facilitating the assembly of CNTs into micro and macro-scale systems. Further, the pellets provide control over the alignment and length of the CNT, attenuating the effects of fluctuating process conditions normally associated with CNT growth. Moreover, nanopellets provide a seeding mechanism whereby CNTs can be grown and subsequently harvested; this enhances control over yield, enabling the fabrication of devices with large areas of high-quality CNTs.

Several fabrication process flows are developed and tested for creating pellets. Actual pellets with embedded CNTs are fabricated and transplanted onto different substrates. The results support the merit of nanopelleting as a means of controlling CNTs, which represents an efficient method for growth and deterministic handling of an individual CNT. Further work on optimized pellet design and linking the nanopelleting concept with assembly methods and actual applications would be useful.

Thesis Supervisor: Sang-Gook Kim
Title: Ester and Harold E. Edgerton Associate Professor of Mechanical Engineering
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Finally, several colleagues were directly involved in this project, including Dr. J.-H. Jeong in processing the CNTs used in this research and Dr. Y.-A. Song in helping initiate the process steps for the revised additive process. These researchers are also responsible for or assisted in capturing the SEM images shown in Figures 14, 16, 17a, 21b, 23, 24, 26b, 32, and 39.
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Introduction

Carbon nanotubes elicited significant attention upon their discovery in 1991 by Sumio Iijima. Since then, there has been keen interest and research covering the synthesis and potential applications of single and multi-walled carbon nanotubes. There remain, however, few feasible techniques for the large-scale manufacture of aligned and geometrically uniform carbon nanotubes (CNTs) [1,2]. Widespread commercial use of CNTs is predicated on the development of robust, large-scale manufacturing techniques. The key challenges to developing manufacturing techniques that enable commercialization can be grouped into three categories: growth, handling, and functionalization.

The nanopelleting concept, devised at the Micro & Nano Systems Laboratory at MIT, seeks to address these challenges. The concept’s main idea is to create a nanostructure, in this case a carbon nanotube (CNT), embedded within a micro-scale pellet shaped to a specific geometry. The concept provides benefits in each of the categories mentioned previously. For growth, nanopelleting utilizes a growth method with controllable alignment, and also provides a mechanism to mechanically control CNT length. For handling, nanopelleting’s key benefit is a shift from the nano to the micro scale, allowing deterministic micro-scale handling and assembly techniques to be harnessed. Nanopelleting is not, however, in and of itself an assembly method, but rather improves the compatibility of nanostructures with deterministic assembly techniques. Finally, with regards to functionalization, the ex situ growth inherent to nanopelleting decouples the growth and use, allowing for high yields of pellets to be harvested and assembled over arbitrarily large areas.

The focus of this thesis is to develop the nanopelleting concept by creating a workable design and suitable process steps, fabricating nanopellets, and investigating the transplanting of nanopellets. The results obtained demonstrate that nanopelleting is a

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1 A patent application, # 60/417,959, has been filed to protect the concept.
viable method of controlling the growth properties and handling of nanostructures, and merits further work for incorporation into devices.

**Background**

Historically, the two known allotropes of pure carbon crystalline structures were limited to planar graphite and three-dimensional diamond crystals. In 1985, Kroto and Smalley discovered C$_{60}$ spheres, known as Buckminsterfullerenes, composed of a network of tri-bonded carbon atoms forming a hollow sphere. In 1991, Ijima discovered that carbon also formed extended tubular structures similar to an extruded C$_{60}$. These tubes were initially observed forming multiple concentric tubes with a hollow core, known as multi-walled tubes, and subsequently also observed to form single-walled tubes. Large tracts of research on these structures has shown them to have remarkable mechanical strength [2,3] (e.g. higher tensile strength than steel), electronic properties (e.g. both conductive and semi-conductive, depending on chiral structure), as well as thermal and chemical properties. These properties have made them of potential interest for a large variety of engineering applications, but no widespread commercial devices that utilize CNTs have yet entered the field.

Prior research on CNTs has focused on several broad areas, particularly the synthesis of and characterizations of CNTs. Most techniques developed to date for large-scale manufacture of CNTs utilize a bulk growth process to produce unpatterned fields of CNTs followed by purification and fluid dispersion to provide high yields of CNTs with no specific geometry or location [4,5]. Alternatively, investigations targeting specific applications utilize in situ growth of CNTs over small areas, and are specific to the application being developed [6-10]. Investigations of synthesis methods or applications of CNTs without controlled or organized growth are less relevant for this research; for example Carbon Nanotechnologies Inc. and Covalent Materials, among others, are selling commercial quantities of nanotubes in the form of soot, with no proposed handling methods for subsequent manufacturing processes.

Those investigations that focus on the organized, large-scale growth and handling of CNTs are interesting, and are reviewed initially below and in more detail in the following...
chapter. Z.F. Ren's group has grown fields of CNTs over glass surfaces up to several square centimeters in area [11], and subsequently grown individual CNTs with controlled location and density [12-14]. This is a promising result, but has not resolved the compromise between creating orderly arrays and growing CNTs over large areas. Several other groups have demonstrated control over the location of CNT growth [8,15,16,17] by patterning aligned CNTs at pre-defined locations on a substrate, but over limited areas. The difficulty of achieving control versus large-scale growth is not addressed by these techniques, again leaving a need for a method that is capable of organized, large-scale growth.

Further, most investigations control the length of CNTs by controlling growth conditions; this produces large variations (on the order of 30%) in the actual length of CNTs. Some work has been carried out to trim CNTs, in particular Agere Systems [18] has developed an interesting method of using a sacrificial locking layer to partially bury nanoconductors then trim the nanoconductors to the desired length. This technique is focused on a particular application, using nanostructures as electrical interconnects, and the broader use of this technique is not addressed within the scope of the patent filings examined. Other researchers have also investigated various handling methods for CNTs, including manipulation of individual CNTs via AFM probe tips [3,19]. Another handling method for CNTs is proposed in the context of large-scale assembly of nanowires using a Langmuir-Blodgett technique [20], but this technique is limited to flat layering of tubes in parallel over liquid films.

Work has also been carried out to apply the organized growth of CNTs to specific applications, such as for IR detection [21], electric circuits [10,22], and field emission [7,23], and nanotube ropes or yarns [24,25]. Several firms are also engaged in research and development of CNT devices. Motorola [26], Samsung, Ise Electronics, and NEC are working on the flat panel displays using carbon nanotubes as emission tips. These techniques all require the organized synthesis and handling of carbon nanotubes; no commercial products have yet been reported from these firms. Other firms developing applications include Nantero, which is working on using arrays of CNTs in nonvolatile electronic memory, IBM for CNT-based ICs, Molecular Nanosystems for sensors and field
emission devices, and Nanosys for opto- and nano-electronics. Much of this work is proprietary and has, with the exception of IBM’s IC research, been poorly reported in the literature.

**Motivation**

Nanopelleting aids in the controlled growth of CNTs by helping define the geometrical properties of CNTs and by decoupling CNT growth from use. By pre-defining the alignment and length of CNTs, nanopelleting improves control over fluctuating process conditions normally experienced in CNT growth. Further, by serving as transport vehicles for nanotubes, nanopellets address the scale mismatch between micro-scale and nano-scale fabrication and assembly, and facilitate the handling of CNTs. Moreover, nanopellets provide a seeding mechanism where CNTs can be grown and subsequently harvested; this enables the deterministic fabrication of devices with large areas of high-quality CNTs. The nanopelleting concept’s benefit, therefore, lies in its strength as a large-scale manufacturing technology that facilitates handling and assembly of CNTs, or indeed of any nanostructure, while also providing control over CNT growth properties and functionalization.

Applications that are particularly well suited to nanopelleting are those that require large expanses of arrayed CNTs with specific, repeated geometries, alignment and location. Examples of such applications include field emission systems for display technology, where even a relatively small display of several square inches would require vast numbers of ordered CNTs. Other potential applications that may be enabled by this technique but are yet under-explored include the use of CNT arrays for pattern transfer using either thermal energy or electron beams, as well as structural applications such as carbon fiber composite interconnects. Moreover, given the broader utility of the nanopelleting concept in terms of multi-scale system design, nanopelleting can be used more broadly as a handling method for a variety of nanostructures and their applications.

**Methodology**

This thesis is primarily an experimental verification of the nanopelleting concept. This verification process started from the first level of defining the functional requirements to be addressed by nanopelleting, on to reviewing potential design solutions, developing
fabrication process plans, and then fabricating and transferring actual nanopellets. The subsequent step of integrating nanopellets into an actual device is not included in this work. The CNTs utilized in this project were synthesized in cooperation with other researchers at MIT and at Boston College, and, while integral to the project, do not represent the primary focus of this work. The bulk of the experimental steps are conducted using standard microelectronics fabrication techniques at several labs at MIT.

Term Definitions
Given the range of terminology used in the literature to represent various issues surrounding CNTs, an upfront clarification is helpful. The three proposed categories mentioned previously (growth, handling, functionalization) are to some extent regularly utilized in the literature, but grouping them in sequence provides a useful framework. These categories are somewhat self-explanatory, but a brief explanation: growth refers to the initial synthesis of CNTs (e.g. via CVD), handling refers to post-synthesis physical manipulation (e.g. length truncation or transplantation), and functionalization refers to post-synthesis steps required to prepare the CNTs for a specific application (e.g. electrically contacting a CNT for a FET). In certain cases, the categories may overlap, particularly for handling and functionalization, but this should not impact the framework's general utility.

The terms controlled and organized growths indicate growth with specific geometry and at predefined locations, including length or diameter. The term large-area growth is used to represent growth over areas necessary for commercial devices, such as displays with areas exceeding 10 square centimeters. Large-scale growth is a similar term, representing the manufacture of CNTs in quantities that would enable standard device applications. While this varies with density, CNT quantities on the order of $10^9$ or more are typical. Finally, micro- or nano-scale specifically refers to a length scale.

Organization of Document
The document is organized to provide a comprehensive review of the design considerations and experimental methods and results. The first chapter reviews the theory, background, and current practices related to the synthesis, handling, and functionalization of CNTs. The second chapter provides an overview of the development of the nanopelleting concept,
including its functional requirements, and the development of the design and process steps. Chapter three provides a detailed review of the experimental steps utilized to fabricate nanopellets. The fourth chapter reviews the results of the various process steps, for a first generation proof of concept design and, in less detail, initial work on a second generation design. The fifth and final chapter is a discussion of the results and areas for future investigation utilizing the nanopelleting concept.
1.0 Theory & Background

The nanopelleting concept offers potential solutions to the current limitations of CNT production in a large-scale manufacturing context. An understanding of the limitations, both theoretical and experimental, helps establish the benefit of nanopelleting. This chapter examines the basic physical structure of CNTs and then moves to a review of the best practices and theory relating to growth, handling and functionalization of CNTs. A linkage of these issues with the nanopelleting concept is then more solidly defined in the following chapter. Further, a brief review of transport phenomena in CNTs is presented to better understand CNTs’ behavior in this domain.

The expectation is not for this section to serve as an underlying foundation for the micro-fabrication processes used to create nanopellets. An entire set of theoretical literature and analytical examinations is relevant for such processes. When appropriate, within the experimental setup or results chapters the theory behind certain processes will be discussed in the context of reaching a particular process solution. Such analyses are not, however, considered central to the novelty of the nanopelleting concept, and accordingly are not reviewed below.

1.1 Growth of Carbon Nanotubes

1.1.1 Structure and Growth Models

Various studies have revealed the structures of single-walled and multi-walled CNTs, including their relation to graphite and fullerene structures [1,2,5,27]. Graphitic carbon is known to contain a carbon atom with \(sp^2\) hybridization bonded to two other carbon atoms, which go on to form a network of planar carbon. A CNT is composed of a rolled-up graphitic plane that has closed on itself. A tube can roll up in a variety of angles along the graphitic plane, influencing the tubes' crystal geometry, or chirality. Examples of two typical structures are shown in Figure 1, with image (a) showing an armchair CNT and image (b) showing a zig-zag CNT. These orientations, along with a variety of intermediate
orientations, are more precisely defined by the exact twist of the honeycomb structure\textsuperscript{2}, and will in turn define whether a CNT is a conductor or semiconductor. Moreover, each honeycomb structure forms a single tube whereas multi-walled tubes are composed of nested concentric CNTs. Indeed, there are also reports of C\textsubscript{60} spheres encapsulated within CNTs to create a peapod-type structure. Controlling the chirality of the tubes is of interest to some researchers, as is the role of encapsulated species (intercalation), but these are not primary issues for this study.

![Image of Armchair (5,5) and Zig-Zag (9,0) structural diagrams]

Figure 1: Side View of Representative Crystal Structure of Typical CNTs

The growth mechanism for the formation of multi-walled CNTs on a catalyst particle is not confirmed. An overall model is described by Ebbesen \cite{27}, with a four step process. These steps are: 1) creation of a metal catalyst seed on a substrate, 2) creation of a carbon source from the decomposition of a hydrocarbon, 3) condensation of the carbon source onto the metal seed particle, and 4) the termination of the tube growth. The third step of this process, in particular, remains a subject of disagreement.

Ebbesen proposes a model whereby the tube structure forms on the exterior edge of the catalyst particle. Ebbesen’s model is similar to the model proposed by Oberlin et al. \cite{28}, who propose that there is no diffusion to the back of a metal particle, but rather that growth occurs by lateral migration of carbon across the exposed surface of a catalytic particle. Baker et al. \cite{29} and Harris \cite{2} outline a slightly different model originally developed for the growth of catalytic carbon filaments. In their model, carbon collects on the top, or front, surface of the catalytic material, dissolves in the metal, and diffuses through to the trailing face due to a thermal gradient, which creates a cone-shaped particle and forms the filament.

\textsuperscript{2} This is the function of the (m,n) parameters, which dictate the exact angle and twist of the tubes. This topic is well discussed by Dresselhaus \cite{1} and Harris \cite{2} and is part of basic CNT structural theory.
A schematic overview of the different models is shown in Figure 2, with Ebbesen’s periphery model in frame a), Oberlin et al.’s surface migration model in frame b), and the Baker-Harris bulk diffusion with a thermal gradient shown in frame c). All these models are developed for filaments, fibers, or tubes that are growing by tip-growth mode, such that the catalyst particle moves up with the growing tube. Further, the size of the particle governs the width of the tubes, albeit lateral migration in the models is also credited with increasing the fiber/tube thickness (for CNTs via the addition of nested tubes).

![Figure 2: Different CNT Growth Models](image)

More recent work by Kuang et al. [30] postulates a mixed surface and bulk diffusion model that links the preferential growth direction of a CNT along nickel’s <110> direction to catalytically active metal faces, with the diffusion on (101) surfaces occurring more rapidly than other surfaces. This model is questioned by Wen et al. [13], who found that CNTs grow inline with the electric field direction of the plasma and not simply along a preferential crystal direction, such that the impact of crystal faces on diffusion and growth direction remains ambiguous.

Albeit different in specific mechanisms, these models converge around the idea of diffusion of carbon in interaction with a catalytic particle. This diffusion mechanism is known as the vapor-liquid-solid (VLS), and is featured explicitly or implicitly in a variety of models. A model for single-walled tubes is mentioned briefly by Charlier and Ijima [1] who believe that the VLS mechanism holds for SWNTs except the catalyst is only a few atoms large, and as such the quantum aspects should be accounted for in the diffusion mechanism. None of the models propose a mathematical model or governing equations, but rather provide empirical observations of the effect of variations in growth conditions. Accordingly, the different growth methods are discussed in more detail below.
1.1.2 Growth Methods
There are a variety of methods for the growth of carbon nanotubes [2,27], including catalytic and non-catalytic methods, a summary of which is provided in Table 1. Among the non-catalytic methods are arc-evaporation, pyrolysis of benzene in a hydrogen environment, and the heating of carbon foils or soot. Catalytic methods for CNT growth, for which the previously discussed models apply, include arc-evaporation, laser ablation, thermal CVD, and plasma-enhanced CVD.

Table 1: CNT Experimental Growth Methods

<table>
<thead>
<tr>
<th>Synthesis Method</th>
<th>Catalyst</th>
<th>Carbon Source</th>
<th>Yield Form</th>
<th>Tube Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc-Evaporation</td>
<td>–</td>
<td>Graphite rod as anode/cathode</td>
<td>Re-condensation on cathode</td>
<td>MWNT</td>
</tr>
<tr>
<td>Vapor cond. – e-beam</td>
<td>–</td>
<td>Graphitic</td>
<td>Condensation on substrate</td>
<td>MWNT</td>
</tr>
<tr>
<td>Vapor cond. – Laser</td>
<td>–</td>
<td>Graphite</td>
<td>Cooled target</td>
<td>SWNT</td>
</tr>
<tr>
<td>Pyrolysis of benzene</td>
<td>–</td>
<td>Benzene Vapor</td>
<td>Graphitic substrate</td>
<td>MWNT</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>–</td>
<td>Graphite</td>
<td>Purified toluene solution</td>
<td>MWNT</td>
</tr>
<tr>
<td>Thermal CVD</td>
<td>Fe/Co/Ni</td>
<td>Methane, ethane</td>
<td>Large arrays on substrate</td>
<td>S&amp;MWNT</td>
</tr>
<tr>
<td>Plasma-Enhanced CVD</td>
<td>Fe/Co/Ni</td>
<td>Methane, Acetylene</td>
<td>Large arrays on substrate</td>
<td>S&amp;MWNT</td>
</tr>
<tr>
<td>Catalytic Arc Evap.</td>
<td>Fe/Co/Ni</td>
<td>Graphite rod</td>
<td>Chamber walls</td>
<td>SWNT</td>
</tr>
</tbody>
</table>

Among these methods, CVD is recognized as being suitable for producing large quantities of CNTs with fairly predictable properties. In particular, plasma-enhanced CVD (PE-CVD) is suitable for high-yield growth of aligned CNTs at temperatures below 700°C on a variety of substrates, including silicon, glass, and even plastic [11,13,31]. While low-temperatures growth is not required for the nanopelleting concept, high-yield growth of aligned CNTs makes PE-CVD the preferred growth method, and it is reviewed in more detail below.

Examples of such work have been reported Z.F. Ren’s group at Boston College, which has grown fields of CNTs over glass surfaces up to several square centimeters in area [11], and subsequently grown individual CNTs with controlled location and density [12-14]. Other examples of interesting CVD research include that by Merkulov et al. at Oak Ridge National Labs [32], Bower, Zhou et al. at UNC-Chapel Hill [33], Wei et al. at RPI [16], Chhowalla et al. at University of Cambridge [34], Fan et al. at Stanford [23], Liu’s group at
Duke University, and others (while not currently focused on CVD growth, Smalley’s group in Rice also has a large body of interesting work).

1.1.3 Plasma-Enhanced CVD
A PE-CVD system has four primary modules: 1) an anode/cathode pair and plasma power source, 2) a heater embedded into the cathode that heats the substrate, 3) a vacuum chamber that controls the system pressure, and 4) a combination of mass flow controllers that feed the required gases. Each of these modules has several key parameters that are varied to alter the properties of CNTs grown. In addition to the main system components, a substrate with a catalytic material is required. This is usually prepared by growing a continuous film on a silicon substrate, although other substrate materials are possible. A schematic diagram of such a system is shown in Figure 3, while a review of the actual experimental system used in this investigation is provided later.

![Figure 3: Schematic overview of PE-CVD system](image)

The key differentiator of a PE-CVD system is its inherent electric field that aids in the alignment of growing CNTs. While the specific mechanism for this alignment is unclear, there is significant experimental evidence supporting this effect. The power supply can be either direct current (DC), microwave, or RF-based. For the case of DC bias, which is most frequently used in CNT growth, a glow discharge is established by applying a bias of approximately 400-800 Volts. The e-field strength and shape depends on the voltage, gas type and pressure, anode-cathode shapes and distance, as well as the substrate temperature [34,35].
For a DC glow discharge plasma, the electric field strength deteriorates with increasing distance from the cathode [27], the characteristic distance of which is known as the cathode fall, or plasma sheath. This distance is estimated to be three times the Debye length ($\lambda_D$) [35]:

$$\lambda_D = \sqrt{\frac{kT_e \varepsilon_0}{n_e e^2}} \quad (1)$$

where $k$ is Boltzmann’s constant, $T_e$ is the electron temperature, $\varepsilon_0$ is permittivity of free space, $e$ is the electron charge, and $n_e$ is the electron density. Chhowalla et al. [34] find the Debye length for a -600V bias with a graphite planar cathode and an acetylene/ammonia gas mixture to be 50-90 $\mu$m. While the specific value can be varied somewhat, the extent of the electric field indicates a practical limitation on quality growth length using such a system.

Another potential limitation of the PE-CVD system derives from the current requirements to maintain proper plasma ignition. The required electric field strength for proper CNT alignment is found by Chhowalla et al. [34] to be at least 0.1 V/μm. Depending on the size and shape of the cathode and the anode, the system’s power supply will need to have sufficient throughput. This places another practical device limitation on the size of the cathode. Even if the plasma uniformly covered the cathode surface, which is not always the case for glow discharges [36], the current requirements for a given voltage drop might drive the power requirement beyond a power supply’s capabilities. Existing 4-inch (100mm) cathode substrate holders employ ~1kW power supplies, such that scaling the substrate would require similar scaling of the power supply; this is not necessarily trivial.

1.1.3.1 Diameter Distribution

The mechanism for CNT formation on initially continuous catalyst films relies on pretreatment within the CVD chamber to create isolated particles from the previously uniform film. The CNTs then grow from the catalytic particles via the mechanisms discussed earlier. Experimental literature points to a clear relation between the diameter distribution of CNTs and the growth conditions. In particular, the catalyst particle size has the most direct impact on the diameter of grown CNTs [1,32,37,38,39]. The particle distribution for a given
catalyst in turn depends on the original film, its thickness, the substrate and any buffer layer, as well as the substrate temperature.

A general theoretical model for the wrapping of graphite sheets to form CNTs is offered by Ebbesen [27] that utilizes the strain energy\(^3\) to predict the internal radius of the CNT, but it assumes that the external radius is determined by the particle size. A model for the formation of catalyst particles is presented by Zhu et al. [40] based on the formation of aggregated free critical nuclei. Their model yields a probability distribution of catalyst particles with reported agreement to CNTs grown by other groups under similar process conditions. The diameter distribution is, nevertheless, difficult to theoretically predict due to the number and sensitivity of process parameters.

Several studies review the impacts of different parameters on the diameter distribution of grown CNTs. Merkulov et al. [32] examine the impact of growing CNTs and nanofibers from nickel dots of varying sizes, with a 10 nm Ti buffer layer and a 15 nm Ni layer on a Si substrate. They find that for dot sizes of less than 350 nm, individual tubes/fibers grow from each dot, whereas for larger nickel patches multiple tubes/fibers grow. Wright et al. [38] examine the role of barrier layers on the distribution of catalyst particles, utilizing TiN and MoSi\(_2\) barrier layers on SiC substrates. They find that the nickel particles retain significantly tighter size variation for the TiN barrier layer, resulting in a tighter variation of CNT diameters. Li et al. [37] investigate the use of ferritin, an iron storage protein to form catalytic iron particles, and grew single-walled CNTs from the particles. Although there were some yield issues, they confirmed that the CNT diameter tracked the nano-particle size distribution. Kukovitsky et al. [39] also undertook a study of the relationship between nanoparticle sizing and CNT diameter by growing CNTs on a nickel catalyst supported on an amorphous carbon substrate. Unlike others, they present a dual state mechanism that depends on the substrate temperature, with growth at 700°C replicating the size distribution of the original catalyst particles, but growth at 800°C resulting in a Gaussian distribution that did not track the initial particle size. They attribute the difference to a change in state of

\(^{\text{3}}\) The relationship is given by Ebbesen as \(\Delta E_{\text{strain}} = \frac{\pi}{12} \varepsilon (r_o - r_i)^2 \ln \left( \frac{r_o}{r_i} \right) \frac{d}{d} \); where \( \varepsilon \) is the Young’s modulus, \( d \) is the length of the cylindrical shell, and \( r_o \) and \( r_i \) are the outside and inside radii, respectively.
the catalyst particle, with the higher temperature producing liquid particles that did not maintain their original sizing; whether this is due to interaction of the catalyst layer and the substrate is uncertain, given that few other studies have used an amorphous carbon substrate.

The creation of catalyst particles is achieved by annealing the uniform catalyst film, typically during the heating of the substrate prior to CVD deposition. Zhu’s theoretical model relates the temperature and film thickness to the resulting particle size. The mechanism for particle formation is a result of minimization of surface energy and mismatches of thermal strains between the substrate and the catalyst film [33,34,36]. The impact of thickness on particle size is supported by the experimental work of Bower et al. [33] working with cobalt, and by Chhowalla et al. [34] working with nickel. The trend in both cases is for thicker layers to form larger particles that in turn produce thicker CNTs, with excessively thick layers adversely impacting growth yield.

1.1.3.2 Length Variation
As grown CNTs can have significant length variation, which may be unacceptable for certain applications. Length control over the tubes is exerted primarily by tuning the CVD flow rates and time; the catalyst particles, however, do influence the yield and length of CNTs as well [41]. H. Dai’s research group [6] has demonstrated very tight length control over aligned CNTs by controlling the growth time, as have Sohn and Lee [7]. An observed limitation on the growth of CNTs for longer times was catalyst de-activation, or poisoning. Bower et al. demonstrate this effect with a cobalt catalyst, where the CNTs do not grow beyond a certain length regardless of processing time; they attribute this to encapsulation of the catalyst within carbon layers that de-activates further diffusion. Catalyst poisoning is also studied by Baker et al. [29] for carbon filaments, who found that treating deactivated catalyst particles with hydrogen led to renewed growth. They found no obvious surface morphology changes of the nickel catalyst particles, but documented renewed growth when acetylene was reflowed in the system.

Chhowalla et al. [34] studied the effect of time and several other parameters on CNT length, with similar results for the effect of time on CNT length. Additional areas studied
included the impact of applied voltage, where increased bias voltages were found to reduce
deposition rates, and pressure, which correlated positively with longer CNT length. They
also examined gas mixture, finding that increasing the acetylene/ammonia ratio from 0% –
100% initially increased length, but for concentrations over 30% seemed to decrease the
resulting CNT length. They propose that the higher acetylene ratios overcome the catalyst
particles' ability to extrude carbon vertically, while resulting in increased lateral growth that
forms pyramidal structures. The final parameter studied by Chhowalla et al. was the
growth temperature, with an apparent optimum temperature for their process at 700°C. At
lower temperatures the growth rate was slower, while at higher temperatures the CNTs
became disordered. Bower et al. [33] observed that the CNT growth rate is inversely
proportional to the nanotube diameter and suggested that the carbon diffusion is constant
for a catalyst particle, which would limit the resultant CNT length from wider particles.

1.1.3.4 Organized Large-Area Growth
Growing CNTs over large areas is required for certain applications, especially display or
patterning technologies where, for example, displays can range from 5 cm in diagonal size
to over 50 cm. The limitation on large-area growth results primarily from practical
limitations on the growth chamber equipment. Establishing uniform plasma conditions
with uniform cathode heating requires sufficient power and robust process control; using
simple power-voltage-current relations it becomes clear that increasing the cathode area
will have a substantial impact on the system’s power handling requirements. Moreover,
once CVD growth is optimized to cover large areas, control over the growth locations must
still be monitored to achieve organized, large-area growth.

While numerous researchers report large-area growth, the term large-area is used rather
broadly to indicate bulk growth rather than macro-scale growth over, for example, entire
wafer surfaces [11,42,43]. A robust manufacturing technique should allow growth over
entire wafers, or even over entire display surface areas, without any deterioration in quality.
Some researchers have reported such growth over die-scale areas [11,44] using PE-CVD, but

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4 That is, given V=IR, P=IV, where the resistance R is dictated by the size of the cathode, such that a halving of the cathode
resistance path for a constant voltage would require a doubling of the current and power requirements of the system.
not over entire wafers. W. Hoenlin et al. reported CVD growth over a 6-inch wafer [45], Lee et al. reported growth over nine-inch FEDs [46] using dispersed films of CNTs, and others report growth over 63 cm² circular areas [47], and over 40-inch diagonal panels [48], although (with the exception of Lee et al.) the exact mechanism could not be determined from the reported information.

Various researchers have utilized templated growth within porous materials to direct the growth of CNTs. Examples include early work by Li et al. at the University of Toronto [49] using nanochannel alumina templates with cobalt deposited at the channel bases, which offered length control over moderately large areas, but limited pattern control. More recently, Jeong and Lee from Postech in Korea [50] and Cao et al. from RPI [51] have reported patterned growth of CNTs within anodic aluminum oxide and tin oxide nanobelts as templates, respectively. Other template materials have also been reported, but while templates can assist in uniform growth over large areas, they are not flexible as a technique for growing CNTs in varying configurations for different applications.

By seeding, harvesting, and then assembling CNTs, rather than growing them in situ, the CNTs can be grown in ideal process conditions and then transplanted. Ex situ PE-CVD growth, similar to the use of arc discharge grown CNTs suspended in solution, overcomes the physical process limitations and couplings of PE-CVD systems while enabling controlled, large-area growth.

1.2 Handling of Carbon Nanotubes
There are no generalized methods, however, for deterministically handling CNTs in large-scale. Assembly of CNTs is currently carried out by either by self-assembly of dispersed solutions of CNTs, or of mechanical handling of small numbers of CNTs. Several research groups attempt the equivalent of handling during the growth phase, including Huang et al. [52] using micro-fluidic channel flow to control the growth of nano-wires, Jung et al. [53] by growing tubes across posts formed on the substrate, Wei et al. [10] by growing CNTs across electrodes in circuits, and others. Interesting work has also been done in developing CNT ropes or yarns [24,25], but this is again highly application specific.
The scale shift central to nanopelleting, where a nano-scale structure is built up into micro-scale structures, provides an alternative handling methodology. The macro-scale carrier can then be handled using self-assembly or mechanical assembly with more ease and control than a simple dispersion of CNTs could, allowing for large-scale handling of CNTs with repeatable control over large areas. The shift in scale does influence the packing of CNTs, but the technique is flexible enough to provide control over the density required for varying applications.

1.2.1 Self-Assembly
Self-assembly in microelectronics and bio-engineering refers to structures that harness chemical or biological interactions to order large-scale structures composed of smaller-scale components. Here we discuss the current practice in self-assembly of carbon nanotubes, as well as recent methods for self-assembly of micro-scale structures.

1.2.1.1 Self-Assembly of Carbon Nanotubes
The reported examples of self-assembly of CNTs involve the use of dispersed CNT solutions that are then selectively adhered to a patterned surface. An example of such a technique for field-emission applications is reported by Oh et al. [54], where purified SWNT bundles in suspension (with a CNT density of 1 g/L) were assembled on the water-substrate-air triple line on pre-patterned substrates at room temperature. The substrates are patterned in two ways, either with hydrophobic coating on glass so that the CNTs would adhere only to the exposed hydrophilic glass, or using metal and octadecyltrichlorosilane (OTS, a self-assembling monolayer) where the CNTs would adhere to the patterned metal.

Similar work by Lee et al. [55] utilizes a self-assembling monolayer of 11-mercaptoundecanoic acid on a gold layer such that the carboxyl groups of functionalized SWNTs attach to the acid. This process is carried out at room temperature on both silicon wafers and polymer films, with field-emission as the target application. Yet another example of this technique is offered by Valentin et al. [56], where aminopropyltriethoxysilane (APTS) is patterned and a solution of SWNT selectively adheres to the APTS.
These self assembly techniques provide basic bulk handling over CNTs, but do not provide a method for deterministically handling individual CNTs or of providing precise alignment of the CNTs. The use of nanopellets enables a variety of micro-scale self-assembly techniques to be utilized for creating large-scale arrays of nanostructures.

1.2.1.2 Self-Assembly of Micro-Scale Structures
Examples of micro-scale self assembly techniques include the use of fluidic self assembly with self-assembling monolayers (SAM), the use of ultrasonic shaker tables with electrostatic force fields [57], and the fluidic self-assembly of tapered microblocks [58]. These techniques, especially that the SAM method, are similar in methodology to the SAM assembly of CNTs, but offer more deterministic control over assembly location. Moreover, such techniques are promising for use in the assembly phase of nanopellets to create large-scale, large-area CNT arrays.

Srinivasan et al. develop a SAM technique [59] (based on work by G. Whitesides) by patterning binding sites on the substrate and corresponding parts using a gold layer followed by alkanethiol precursor molecules to render the gold hydrophobic. The patterned substrate (now with alternating hydrophobic/philic regions) is then dipped in a bath with a hydrophobic adhesive floating on water, which coats the binding sites. Finally, a pipette directs the micro-scale parts toward the substrate, where binding and shape matching occurs due to interfacial free energy minimization. They report assembly of micro-blocks with size ranges of 150 – 500 \( \mu m \) with alignment precision of less than 0.2 \( \mu m \) and rotational misalignment of less than \( \sim 0.3^\circ \).

Another interesting fluidic technique is developed out of J. Smith’s group in UC Berkeley, now commercialized by Alien Technologies. This technique uses a suspension of integrated circuits (or other electronic devices) on specifically shaped blocks that are dispensed onto a substrates that has the reverse shapes of the blocks. The acceptor substrate and the block will favor mating into predetermined positions, which is encouraged by inducing vibration in the substrate. The reported sizes of such blocks are in the range of 10 – 185 \( \mu m \) with orthogonally correct alignment on the order of \( \pm 1 \mu m \). Further details on this
technique are not published as part of the white paper and patent filing related to this technique.

Another technique that utilizes a vibrating table is developed by K. Böhringer [57], where ultrasonic vibration is used to overcome friction and adhesion and an electrostatic force is used to lock parts into place once they reach their desired locations. So far these experiments have been on macro-scale parts, but this technique could be extended into the micro-scale domain. Such methods, especially with further work to increase alignment precision, offer very promising routes for deterministic assembly of nanopellets.

1.2.2 Mechanical Assembly

There has been some research into the mechanical manipulation of CNTs [3,19], primarily by using an AFM tip. This is a highly limited technique, both in control offered and its scaling capabilities. Another example of such work is via x-y-z nano-manipulators built within a scanning electron microscope [60,61]. Such methods are rather cumbersome, and more importantly, represent serial methods that would be ineffective for large-scale assembly. Accordingly, even with the scale shift offered by nanopelleting, mechanical assembly is less preferable to self-assembly. A simple calculation can serve to illustrate: for a substrate with 100 nm diameter tubes spaced 300 nm apart, there will be \(3.33 \times 10^4\) tubes per cm, or 1.1 billion nanotubes per square centimeter. Such large amounts of CNTs require techniques that can offer high yields with minimal user interference.

1.2.3 Trimming

There are multiple methods reported for trimming of CNTs as part of their integration into devices, including the use of mechanical fracture and high-energy beams. Typically CNTs are trimmed either to remove catalyst particles (purification) or to achieve a specific geometrical conditions. Researchers at Agere [18] have developed a technique for trimming by partially burying CNTs in a sacrificial layer then mechanically trimming via chemical etching or mechanical polishing. A similar technique (also for electrical interconnects) is developed by Li et al. at NASA Ames Research Center [62], whereby SiO\(_2\) is deposited to encapsulate the CNTs that are then trimmed using CMP. An interesting laser trimming
technique is reported by Cheong et al. [63] who use a directed laser beam to truncate the length of CNTs only in selected areas, creating a pattern of short and long tubes in an original field of CNTs.

1.3 Functionalization of Carbon Nanotubes

Functionalization of CNTs refers to the post-growth steps required to adapt or enable a CNT for a particular application. Differing applications each require the functionalization of CNTs in a different manner, such as the purification of CNTs (removal of catalyst particles and amorphous carbon), adherence to a surface, intercalation, and other chemical modification of the CNT structure [4]. Some of these steps could be classified as handling steps (alignment, trimming), but functionalization remains an important part of developing applications of CNTs.

1.3.1 Connections & Anchoring

A large amount of prior work has developed techniques for functionalizing CNTs with carboxyl or other groups for adhesion to a substrate as part of an assembly method. Connection of CNTs to substrates post-growth is also needed in other contexts, such as IBM’s CNT transistor. In that case, a CNT is bridged across two gates, and metal is deposited to form an electrical connection. Various other groups have investigated the connection, or anchoring of CNTs, including Dohn et al. [64] who use deposited gold to solder CNTs onto silicon and Ziroff et al. [65] who use a focused ion beam microscope to locally deposit platinum contacts. Such work is interesting for use in developing specific applications.

1.4 CNT Transport Phenomena

Transport though CNTs is of interest for a variety of applications, including traditional transport such as thermal and electrical or even transport of gases, liquids, and other energy beams (light, x-ray, etc.).

Electron transport is the most widely discussed, especially since CNTs are hypothesized to exhibit ballistic transport of electrons (electron conduction with no resistance or dissipation), and experimental work supports this phenomenon [2]. Imperfections,
junctions, and interconnections within the CNT will impact this, and this is subject to considerable study [1]. Moreover, the chirality of the CNTs influences the electrical behavior. Frequently such structural imperfections and electrical connections limit the theoretical electron transport.

Studies of thermal transport within multi-walled CNTs differ on the accounts of room temperature conductivity. Dressehlaus et al. [1] indicate that the conductivity is phonon dominated, nonlinear, and equal to ~ 25 W/m·K @ 300°K, smaller than for carbon fibers. In a differing estimate, Kim et al. [66] observe the conductivity of MWNT to be greater than 3000 W/m·K, also at room temperature.

As for single-walled tubes, the thermal transport of an individual single-walled nanotube is reported to be on the order of 200 W/m·K [1] @ 300°K. Thermal conductivity of SWNT bundles is significantly lower, on the order of 5 – 35 W/m·K [67] at similar temperatures.

With regards to optical transport, IBM reported heated CNTs emitting infrared light energy; this is simply luminescence and not actual optical transport through the CNTs. Others have, however, reported actual light emission through the tube [1], but this remains poorly understood.

Gas and liquid transport has also been investigated through CNTs. Gas transport is typically reported within the field of gas storage [2], including hydrogen and argon storage in tubes. An example of liquid transport is reported by Berezhkovskii and Hummer [68], who provide theoretical and simulation results for single-file transport of water molecules through CNTs.
2.0 Nanopelletting Concept Development

2.1 Birth of the Nanopelletting Concept

As discussed in the previous chapter, there are a variety of methods in use for growth, handling and functionalization of CNTs. These methods are fairly successful at addressing portions of the various challenges facing CNTs, but do not represent generalized strategies for CNTs in the context of large-scale commercial fabrication. The nanopelletting concept was devised as a potential manufacturing technology for CNTs by Professor S.-G. Kim at MIT. The nanopelletting concept’s main idea is to create a nanostructure, in this case a carbon nanotube (CNT), embedded within a micro-scale pellet shaped to a specific geometry.

The concept provides benefits in each of the categories mentioned previously. For growth, nanopelletting utilizes a growth method with controllable alignment, and also provides a mechanism to mechanically control CNT length. For handling, nanopelletting’s key benefit is a shift from the nano to the micro scale, allowing deterministic micro-scale handling and assembly techniques to be harnessed. Nanopelletting is not, however, in and of itself an assembly method, but rather transforms nanostructures into easily assembled units. Finally, with regards to functionalization, the ex situ growth inherent to nanopelletting decouples the growth and use, allowing for high yields of pellets to be harvested and assembled over large areas. That it, nanopelletting plays a seeding role for CNTs, where the tubes are grown in optimal conditions, modified as necessary, and then assembled over larger areas and in larger scales than possible using in situ techniques.

Nanopelletting is conceptually a useful tool in the large-scale fabrication of CNTs, providing a generalized manufacturing compatible technology. The next step is to develop a workable plan and fabricate prototype pellets to prove the basic concept, which is the goal of this thesis. The first steps in the translation of the concept into physical reality are discussed next.
2.2 Process Design

2.2.1 Functional Requirements
The first step in developing the nanopelleting concept into a workable design was to determine the functional requirements. The functional requirements developed are shown in Figure 4 below. These functional requirements were initially conceived as a broad set of concepts by researchers at the Micro and Nano Systems Laboratory at MIT; the structure below formalizes those concepts into specific requirements.

The functional requirements (FRs) are broken down into first through third-level requirements, with each level elaborating more detail on the FR level above it. The first FR, decoupling of the growth and use of CNTs the main theme of this concept, and is similar in concept to the seeding and harvesting of grass. By eliminating the necessity for in situ growth, decoupling allows for mass production of CNTs with pre-defined characteristics that can then be grown, handled, and assembled at point of use.

In keeping with these desired benefits, the second level of functional requirements breaks down into three main areas; first, the growth of CNTs in bulk; second, the creation of a micro-scale carrier for the CNTs; and third, the transplanting of the carrier to point of use. These requirements are similar to the previously discussed categories of growth, handling, and functionalization; the third requirement, positioning at point of use, bridges handling and functionalization, and is to a large extent application specific.

The third-level functional requirements, similarly, flow from the three second-level requirements. The requirement for mass growth of CNTs is linked to the large scale of this technique; accordingly the growth technique should be capable of quickly growing large
quantities of straight, aligned CNTs either in clusters or as individual tubes. An optional FR for the nanopellets is to control the growth length of CNTs; this is application specific and accordingly is shown within a dashed-line box. Control over diameter and chirality might also be required for certain applications, but are not currently within the scope of the concept.

The CNT carrier bridges multiple scales by embedding the CNT within a larger pellet; but the pellet’s effectiveness as a carrier depends on its capability to grab and release the CNTs. That is, the fabricated nanopellet should be releasable from the original growth substrate along with the embedded CNT, and once transplanted the pellet body material should be selectively removable from around the CNTs.

These two stages are illustrated in Figure 5, from left to right, such that the pellet as fabricated and embedding the CNT is released cleanly from the original substrate without damaging the CNT, and is subsequently positioned at point of use and (if desired) the pellet body filler is removed without damaging the CNT.

2.2.2 Design Parameters
The functional requirements serve to define the issues that a manufacturing process should address, similarly design parameters (DPs) that provide the physical and manufacturable embodiments of the FRs are developed. Note that while the language of FRs and DPs derives from axiomatic design principles, a detailed axiomatic design review is not the goal. Rather, this approach provides a useful high-level framework to develop physical design solutions. Within this framework, DPs are developed by systematically mapping from the first, second, and third level FRs. As with most design processes, especially for nascent products or techniques, this is an iterative process that may not settle on all the ideal methods on the first pass.
The first-level design parameter, as shown in Figure 6, is a reflection of the design target, nanopelleting, and does not directly reflect a physical attribute, the second-level design parameters do, however, begin mapping into the physical domain. The second-level DPs are 1) CVD for CNT growth, 2) pellets acting as the carriers, and 3) self-assembly being a potential method for large-scale positioning at point of use. These physical processes are, at this stage, sufficiently broad to encompass a variety of process variations, and would not change significantly depending on application. Indeed, these processes represent the core physical processes for nanopelleting.

The third-level DPs are more variable, such that the specific physical embodiment depends on the particular application. For example, an application may require clusters of CNTs rather than individual tubes, accordingly the catalyst patterns will either be sub-micrometer patches patterned using non-optical techniques, or micrometer-scale patches patterned with optical techniques. This variability carries on to the pellet design, where a different pellet material will impact etch chemistries for selective release, as well as on to the assembly and anchoring techniques. To work around this variability, a generic application was considered while developing proof of concept DPs and translating them into an actual process plan. This is further simplified by the limited interaction between CNT growth techniques and the two latter steps, so that an optimum growth process can be uniformly used while varying the pellet design and assembly methods.

Utilizing a generic application as a base, the third-level DPs shown in Figure 6 are developed by considering the possible design embodiments and selecting the ones conceived as most likely to yield the desired results. Sub-micrometer catalyst patches can be used to create individual tubes, while the use of PE-CVD helps to ensure aligned growth. Length uniformity, if needed, can be achieved by chemical mechanical polishing of the
substrate and pellets to trimming the embedded CNTs. Selective etching or removal of materials is regularly done in microelectronics, and picking the substrate and pellet material in combination with the etch chemistries allows control over this step. For example, using a silicon substrate and an epoxy polymer for the pellet, xenon di-fluoride (XeF₂) and oxygen plasma etching (ashing) can be utilized for selective release of the pellet and removal of the pellet material, respectively (these two DPs are shown with an asterisk to denote the possible variation). Finally, for assembly, the third-level design parameters that satisfy self-assembly could be either of self-assembling monolayer [59] or pellet blocks that are compatible with fluidic assembly similar to that achieved by Alien Technologies [8]. The best DP for anchoring is to use the pellet body, but if the pellet body needs to be removed for other purposes then an appropriate anchor layer is a viable and necessary DP.

2.3 Process Flows
Defining the functional requirements and design parameters created a set of specifications for what the physical processes need to achieve and recommended broad approaches; the next step in developing a fabrication work plan is to develop process flows for the various steps. This is similar to process flows developed for machining of standard mechanical items, as well as to the process plans typically developed in microelectronics fabrication. In such cases, there are typically multiple process flows that can arrive at the same end point, which is also the case for nanopelleting. Two possible process flows are discussed below: a subtractive process that utilizes substrate trenches as molds for pellets, and an additive process that creates pellets by building up onto substrates.

2.3.1 Subtractive Processing Flow
The process shown in Figure 7 lays out the subtractive process flow, which is the original method developed to fabricate nanopellets. The term subtractive process is used given the etching of the substrate that removes material to form molds where the pellet blocks can be cast. A nanopellet requires the growth of aligned CNTs embedded within blocks of uniform geometry, which in this process are then planarized, selectively released from the original substrate, and assembled in their final location. The steps shown also represent the major
process steps required for nanopelleting, and track the experimental steps required to create a nanopellet.

The first step of the process is to etch trenches into a substrate that act as molds for the pellet filler material. The use of trenches as a mold helps to ensure geometrical consistency, and also provides an etch stop point for subsequent planarization. The second step is to pattern a catalyst and, if necessary, an appropriate buffer layer at the bottom of each trench. The buffer layer can also be used as an anchoring layer, which would be required if the pellet body is removed as shown in the final step. The catalyst will then nucleate the growth of nanotubes, which is the third step of the process. Step four is the pouring of the pellet filler, which can be a variety of materials that meet the selectivity requirements for pellet release and removal. Step five is the planarization of the filled pellets, creating isolated pellets of uniform geometry with embedded CNTs. Step six is to release the pellet from the substrate by etching away the silicon, followed by step seven, the transfer of the pellets to a receptor substrate. An optional eighth step is the removal of the filler material, as demanded by the application; this would leave an exposed CNT on the receptor substrate.

Figure 7: Subtractive Process Fabrication Flow for Nanopellets

Benefits of an additive process include the use of the silicon to act as a mold for geometrical consistency of the pellets as well as an etch stop for the planarization. The process does require the growth of catalyst patches at the bottom of trenches; depending on
the geometry of the trench this could be challenging. Another potential challenge with this process is the growth of CNTs within trenches that are narrow and deep using CVD.

The majority of the steps can be carried out using standard integrated circuit and MEMS fabrication techniques available at the Mircosystems Technology Laboratories at MIT. Self-assembly methods and detailed investigations of pellet transfer are beyond the scope of this thesis, but might be useful components of attempts to link this technique to an actual application of CNTs. A review of the experimental setup of the various steps is given in the following chapter.

2.3.2 Additive Processing Flow

The process shown in Figure 8 lays out the process flow for additive processing, the next design iteration of nanopellets. The main difference between the two techniques is a shift from subtractive processing where trenches are etched in silicon to a process where pellets are additively built up onto a silicon wafer. In the original design, the trenches served as molds for nanopellets, which helped to ensure a particular geometrical shape, but increased the complexity of the manufacturing process. In the next generation process flow, the CNTs are grown on flat substrates and subsequently coated with a suitable polymer, simplifying the patterning of the catalyst patches and reducing the number of process steps.

![Figure 8: Additive Process Fabrication Flow for Nanopellets](image)

Further, this revised process avoids the need for mechanical polishing of the substrate to isolate the pellets, and instead utilizes standard patterning techniques in polymers such as SU-8 to create high aspect ratio pellets with repeatable geometries. Given the elimination of
the CMP step, uniform trimming of CNTs is not a feature of this process, which might impact certain applications. By layering multiple types of polymers, the pellets can effectively be composed of multiple layers that can then be selectively removed as required.
3.0 Experimental Setup

The processing flows discussed in the previous chapter require the use of a variety of steps, each requiring different combinations of apparatuses, materials, and procedures. This chapter describes the experimental tools and setup used to conduct the various experiments. Experimental results are described in the following chapter. Given that the subtractive process represents the original process used to prove the nanopelleting concept, its steps are developed more fully than those for the additive process flow. Common to both processing flows is the use of a plasma-enhanced chemical vapor deposition for CNT growth. Accordingly, this is the first experimental step reviewed, after which the subtractive then additive setups are discussed.

3.1 Nanotube Synthesis

The growth of carbon nanotubes used in this research was carried out by a post-doctoral researcher from the Micro and Nano Systems Laboratory group. For initial growth as part of the subtractive process flow, we collaborated with Professor Z.F. Ren of Boston College to utilize his group's PE-CVD system. Over the past academic year the aforementioned post-doctoral researcher has also undertaken construction of a PE-CVD system at MIT, which is expected to be complete by summer of 2004. CNT growth for the additive process flow will be carried out once this chamber is completed.

The PE-CVD systems located at Boston College and under construction at MIT are similar in design. They are both direct-current plasma-enhanced CVD chambers similar in function to that described in section 1.1.3. The feedstock can be varied, but is designed to be a mixture of acetylene and ammonia gases, utilizing a nickel catalyst. The gases are flowed into the chamber through a gas ring above the cathode surface. The substrate temperature is adjusted between 500 and 1000°C by controlling a heater unit embedded in the cathode. The cathode is connected to the direct-current power supply, which is controlled to reach proper plasma ignition at varying pressures. A photo of the MIT system being built by the post-doctoral researcher is shown in Figure 9.
The tubes grown by the post-doctoral researcher are taken as is, and the exact process parameters are not elaborated as part of this thesis. Further, given the prior work by others in documenting the capabilities of such a system to grow multi-walled CNTs, detailed investigation of the inner structure of the grown tubes is also not conducted. The central aspect of this thesis is the development of the nanopelleting concept for handling and manipulation of nanostructures, and CNTs in particular. Accordingly the focus of the various experimental steps is primarily on those process steps related to building a pellet, and these steps are discussed next.

3.2 Subtractive Processing Flow

3.2.1 Trench Fabrication
There are two primary methods utilized for the fabrication of trenches on the silicon substrates, reactive ion etching (RIE) and potassium hydroxide (KOH) anisotropic etching. Both of these steps are carried out in the Microsystems Technology Laboratories (MTL) at MIT. RIE should result in trenches with relatively vertical sidewalls and KOH etching will result in preferentially etched trenches with sloping sidewalls.

An overview of the RIE process steps is shown in Figure 10. The RIE machine is an Electron Cyclotron Resonance enhanced Plasmaquest unit. The process chemistry is a
standard silicon etch recipe of 5 sccm O₂ and 50 sccm SF₆ with a pressure of 100 mTorr, a chuck temperature of 25°C, 400 W of power and 20 W of RF bias. The masking pattern is OCG 825 positive photoresist spun to 1 μm thickness with an HMDS adhesion promoter applied in an oven prior to spin coating. The photoresist is pre-baked at 90°C for 30 minutes, then patterned using an Electronic Vision EV620 Mask Aligner with a 350W mercury bulb at 365-405 nm wavelength, with a standard chrome-on-glass mask produced by Advance Reproductions Corporation. The photoresist is developed in an OCG 934 1:1 until visual completion then post-baked at 120°C for 30 minutes. The RIE rate governs the time required for trenches of various depths, and the machine’s particular rate was used as a initial estimate. The trench size is variable, and is controlled by the patterned mask, which in this case had trenches that ranged in size from 10 to 100 μm, both square and circular.

KOH etching is a slightly more complex liquid etch that results in preferential etching along the <100> direction exposing the {111} planes. An overview of the process steps is shown in Figure 11. The first step in this process is to pattern a hard mask, either out of silicon nitride or thermal oxide, the latter is used for our experiments. N-type test (100) wafers are RCA cleaned with an HF dip, inserted into a Thermco furnace on quartz wafer boats for 3 1/3 hours to grow a 1 μm conformal oxide layer. The oxide is then patterned with a positive resist patterned on the EV620 aligner using a transparency mask printed by the Photoplot Store, Colorado Springs, CO and developed to expose the oxide to be removed. The oxide is etched with a 10 minute dip in a 7:1 HF Buffered Oxide Etch, after which the photoresist is removed by ashing in an IPC/Branson Barrel Asher with a 1200W 13.56mHz RF power supply. Once the hard mask is prepared, the wafers can be KOH etched in a wet bath with a 25 percent by weight solution of KOH pellets and de-ionized (DI) water at 80°C. The observed etch rate is 80 μm per hour, and the etch time depends on
the desired etch depth; in this case the trenches are designed to be 15 μm wide, with a 10 μm deep etch that requires ~7.5 minutes.

![Figure 11: KOH etch experimental sequence](image)

**3.2.2 Buffer and Catalyst Layer Deposition**

Catalyst and buffer metal layers are deposited via liftoff of an e-beam evaporated metal film. There is the option of using different metals and of stacking multiple layers where the first acts as a buffer layer and the second acts as a catalytic layer. This is controlled by varying the type and order of deposited metals. Several metals [69] can be used as the catalytic material for nucleation of CNT growth in a PE-CVD chamber. We use nickel films, with thicknesses of 15-50 nanometers as the catalytic material. The size and shape of the nickel film governs the growth of the CNTs, a conformal, uniform film will result in a field of CNTs. Patterning the film will result in smaller patches of CNTs restricted to areas with exposed catalytic material.

The first step of the process is to coat and pattern a photoresist, after which the metal layers can be deposited via sputtering or electron-beam evaporation, following which the resist is stripped leaving the designed metal patterns.

Patterning of catalytic layers with micrometer-scale features is carried out using optical lithography. This is achieved by coating a standard 4-inch n-type wafer with an AZ 5214E image reversal photoresist. After coating, the resist is pre-baked for 30 minutes at 90°C, exposed on the EV620 with the mask pattern in place for 2 seconds, post-baked for 30 minutes at 90°C, flood exposed for 45 seconds, then developed in AZ 422 for 2 minutes. We utilize a second mask for the catalyst layer with alignment marks that correspond to those etched in the previous trench fabrication step. Liftoff is carried out in an acetone bath until visual completion.
Patterning of catalytic layers with sub-micrometer features is carried out with scanning electron beam lithography. The SEBL system is located within the Research Laboratory for Electronics at MIT, and is a 50 keV VS26 system. The resist is a PMMA (poly-methyl-methacrylate) positive resist spun to a 200 nm thickness. The beam was set at scan speeds between 0.45 - 0.75 MHz and dosages between 597 - 358 μC/cm². The system resolution is determined by the field size, but 100-200 nm features are well within its capabilities. The PMMA is developed in a 2:1 2-propanol:MIBK (methyl-iso-butyl-ketone) mixture at 21°C; after metal deposition liftoff is carried out using a heated NMP (1-methyl-2-pyrrolidinone) bath at 95°C.

Once a certain design is established and developed, the serial patterning carried out with e-beam lithography could be transitioned to x-ray lithography or zone plate array lithography, parallel sub-micrometer patterning techniques developed at MIT's NanoStructures Laboratory (NSL). These would allow significant rate and cost improvements in large-scale patterning of catalyst patterns. Other techniques exist, including interference lithography [70,71], but a sequence of e-beam and x-ray is favored as it allows initial design flexibility followed by parallel batch fabrication with arbitrary distance between features.

3.2.3 Filler Material Casting
The first challenge of casting, or spin coating, the filler that forms the bulk of the pellet is to select an appropriate material with the desired functional properties. That is, the pellet must withstand removal from the silicon substrate, and after the pellet is positioned at point of use, the filler should be selectively removed without affecting the CNTs. This is complicated by the need to spin, or cast, the filler material over wafer pieces\(^5\) (1x1 cm) and the need to coat sufficiently thick layers to ensure that all topography was uniformly coated. Initial testing on two materials, spin-on glass and M-Bond™ 610 epoxy-phenolic resin from Structure Probe, Inc., revealed that the M-Bond is better suited to forming uniform layers on

\(^5\) For the CNTs grown in the PE-CVD chamber of Prof. Ren of Boston College, the full 4-inch wafer is cut into dies after catalyst liftoff. While the system's cathode could handle pieces of 4-inch wafers, better experimental results were achieved using small 1x1 cm pieces due to temperature variations across the cathode surface. The MIT system has a 4-inch cathode with dual-zone temperature control, which will be tested with full wafers once completed.
small wafer pieces without stress-induced cracking during curing. Further tests showed the M-Bond to be resistant to acetone as well as XeF₂ etching, yet susceptible to O₂ plasma ashing, satisfying the specificity requirements for the pellet filler.

The M-Bond is cast onto 1x1 cm wafers mounted onto a ½ cm vacuum chuck in a Headway spinner. A pipette is used to control the application of a small amount of M-Bond in a static dispense so that the wafer surface is covered with material. The spinner is immediately started at 500 rpm for 5 seconds, followed by 1500 rpm for 25 seconds. After spinning, the substrates are cured on hot plates set to 150°C for 1 hour, after which they are ready for planarization.

3.2.4 Chemical Mechanical Planarization
Chemical mechanical planarization (or polishing) is conducted on an in-house system at the Laboratory for Manufacturing and Productivity (LMP) at MIT, a photo of which is shown in Figure 12. The machine has dual rotors with a 4-inch chuck and a Rodel IC1400 pad mounted onto the lower platen, and Cabot iCue 5001 alumina-based slurry is pumped onto the pad surface. The chuck has a rubber surface with no vacuum capability; accordingly the substrates are mounted onto the chuck using by wetting the backside with DI water such that thin film adhesion keeps them in place.
The two process parameters varied are the spin speeds and the pad force applied, in this case we used rotor speeds of 50-75 rpm, and pressures from 5-10 psi. The process has no specific end point detector, and the substrate is removed every 5-10 minutes and inspected under an optical microscope to confirm process completion.

3.2.5 Pellet Release
Pellets are released via surface machining of the silicon with XeF₂. As discussed in the earlier section on filler material casting, M-Bond 610 is found to be resistant to exposure, allowing the XeF₂ to selectively etch underneath the epoxy and release the pellets. The system utilizes a solid XeF₂ source, an expansion chamber, and a main etch chamber. The etch rate varies between 3 – 6 μm per minute, and an etch time of 12 – 15 minutes is used to release the pellets.
3.3 Additive Processing Flow

Several of the process steps for the additive process flow are identical to those from the subtractive process flow, including catalyst layer deposition, CNT growth, and pellet release. Accordingly, these are not discussed again. Further, the planarization step is actually not required in this process flow, given that isolated pellets can be formed by patterning polymer layers down to the silicon substrate surface. The steps that are particular to this process include the formation of polymer layers onto a flat substrate, followed by the patterning of the polymer to form isolated pellets; these two processes are described further next.

3.3.1 Polymer Layer Formation

The choice of polymer material is simplified by the large amount of prior work on patterning polymer layers applied onto silicon substrates; polymers such as SU-8 and polyimide are regularly utilized in MEMS research. Creating multiple layers is considered an optional step in creating pellets, but is described here for completion. The experimental sequence for application of SU-8 and polyimide is shown in Figure 13, and described below.

![Figure 13: Polymer Layer experimental sequence](image)

The first step of this process is to piranha clean (1:3 H₂O₂:H₂SO₄) fresh wafers twice for 10 minutes each, followed by spin drying and a dehydration bake at 200°C for 5 minutes. The next step is to apply the polyimide by spinning it from a static dispense with a 5 second spread cycle and a 30s spin cycle at 2,500 rpm to obtain a ~ 8 µm thick layer. The PI is baked at 350°C for 60 minutes in a tube furnace. SU-8 2075 from MicroChem Corp. is spun to 130 µm thickness and pre-baked using the using the manufacturer’s specifications.
3.3.2 Pellet Patterning

Pellet patterning is carried out in two stages, first by developing the SU-8 using a standard bake-develop-bake cycle, then by etching the polyimide in a plasma etcher. In the first step, the SU-8 layer is exposed on the EV620 system with a chrome mask for four 20 second intervals with a five second wait time. The chrome mask pattern consists of arrays of 20 μm circular patterns, two arrays with 50 μm periodicity and two with 100 μm periodicity. The mask is produced from a transparency film original (printed by the Photoplot Store), which is patterned from a chrome blank. After exposure, the SU-8 is baked and developed in PM Acetate following the manufacturer’s recommended times.

The polyimide layer is etched by utilizing the patterned SU-8 as a hard mask and placing the wafer into the same ECR system described earlier for RIE of the trenches. A different chemistry is used, consisting of 70 sccm of O₂ and 15 sccm of CF₄, with a pressure of 50 mTorr, 400 W of power and 10 W of RF bias; the wafer is exposed in this environment for 20 minutes to complete etching the PI.
4.0 Fabrication Results

The objective of this research project was to convert the basic concept behind nanopelleting into a physical reality. Accordingly, the goal of the work was to fabricate actual CNT-bearing nanopellets and demonstrate their release and transfer from the original growth substrate to a new, acceptor substrate. The results obtained favorably support this objective, indicating that the nanopelleting concept is viable as a manufacturing technology and that further work on the technique is worthwhile.

This chapter discusses the various elements that go into the process and the results for each. The first section discusses the results for catalyst patterning, both micrometer and sub-micrometer sized. The second section briefly discusses the results for CNT growth, which are mostly conducted by other researchers but are presented in basic form for completion. The third section discusses the subtractive process flow results, including trench etching, filling, planarization, and pellet release. The fourth section discusses the additive process, for which there are initial results of polymer coating and patterning. The final section discusses the issue of transplanting of nanopellets, including initial attempts at transfer into organized patterns and anchoring of the CNTs once the pellet filler is released.

4.1 Catalyst Patterning

4.1.1 Micrometer-Scale Patterning via Optical Lithography

Micrometer-scale deposition and patterning of catalyst patches is carried out using optical lithography and liftoff as described previously, and was mostly carried out by an undergraduate research aide. An image of the nickel patch is shown in Figure 14, taken in a Philips XL30 environmental SEM. The patch shown is 5 µm in diameter, and is ~ 15 µm thick. Micrometer-scale patterning of metal films is a well understood process, and accordingly is not discussed further.
4.1.2 Sub-Micrometer Patterning via e-Beam Lithography

Part of our investigation has focused on getting individual CNTs to grow from a catalyst patch; accordingly patterning of sub-micrometer nickel patches is necessary. We have successfully produced catalyst patches in the 115-220 nm diameter range on a flat wafer surface as shown in Figure 15. The figure shows a pattern (a) of 200nm nickel circles (b) that have been patterned on a bare silicon surface using the e-beam writer with a 200nm thick PMMA resist and e-beam deposition and liftoff of a 15 nm thick Ni layer. The images are taken on a Zeiss SEM. The circular shape is patterned by writing square patterns with 200nm nominal sizes where the sharp corners are effectively blurred in the patterning process.

Figure 15: Nanopatches of nickel catalyst on silicon substrate

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6 As shown by Ren et al. [11] and Merkulov et al. [32], CNTs will grow as individual tubes from catalyst patches in the diameter size range of 200 nm.

7 Image (a) is a low-magnification view of image (b), and while missing a scale bar, the scaling can be generally perceived from the scale bar of image (b).
We were able to pattern circular patches as small as 117 nm in diameter using this technique by designing 150 nm nominal sized squares. A less noticeable change was achieved from 175 nm nominal sized squares, which resulted in 167 nm sized patches. Further, we did observe some variation in patch size for similar nominal sized squares, primarily the result of changes in dosage while optimizing the process.

4.2 CNT Growth
The next step of the investigation was the growth of aligned multi-walled CNTs via PE-CVD. As discussed in the previous chapter, all the CNTs used in this research have been grown at Boston College by a post-graduate researcher also working on the nanopelleting project. Accordingly, a detailed discussion of the growth parameters and results is beyond the scope of this thesis. A brief summary of the overall results for the CNTs used in this research are, however, discussed for completion. The CNTs used and shown were grown between February and June 2004; no CNTs have been grown yet from the CVD system at MIT.

Two examples of the resulting multi-walled CNTs are shown in Figure 16 (a) and (b). The CNTs in image (a) are grown on a 15 nm thick nickel layer on silicon, while those in image (b) are grown on 15 nm nickel film on top of a 20 nm buffer layer of SiO₂ on silicon. Otherwise, the processing conditions are the same, with a working pressure of 8 Torr, flow of 80 sccm of acetylene and 160 sccm of ammonia, a plasma voltage of 515 V, and an estimated cathode temperature of 600°C. The two samples are grown for 10 minutes, after which the acetylene flow is stopped, the chamber is cooled down slowly, and the samples removed.

The CNTs exhibit tip-growth mode, with Ni spheres at the tips of the CNTs that are visible as bright spheres at the tip of the tubes. The tubes grown on nickel without a buffer layer are noticeably thicker than those grown on a SiO₂ buffer layer. This is likely the result of a smaller average particle size formed during annealing on a buffer layer. The CNTs are well-aligned, with an average thickness of 200-300 nm for those in image (a) and 100-200nm for those in image (b). The density of CNTs is approximately 2.1x10⁸ per cm² for the CNTs of image (a) and 3.2x10⁸ per cm² for image (b). The height of the CNTs depends on the
processing time, and while the average tube height is similar for the two samples, there is some height variation within each sample. The cause of the slight taper is not explored via detailed TEM study, the cause could be either etching of the nickel particles that decreases the resulting tube size as they grow, or the deposition of amorphous carbon around a multi-walled tube.

The thicker tubes should be the result of additional stacking of concentric or tubes, such that the thicker tube has more walls. We did not perform TEM cross sectional analysis to determine the exact structure of the tubes; given the focus on creating nanopellets, the exact internal structure is not central to this study. Finally, given that the sub-micrometer catalyst patterns were created after collaboration with Boston College ended, there are no results for growth of individual tubes, although this is considered an important direction for future work on this project.

4.3 Subtractive Process Flow

4.3.1 Trench Etching
Trenches are etched into fresh silicon wafers using reactive ion etching or KOH etching. The size of the trenches is controlled using an appropriate mask, and the etch depth is controlled via the process parameters. An example of an etched trench with a catalyst patch at its center is shown in Figure 17-a). The trench shown is circular, with a 100 µm diameter and a 2 µm depth. A square trench is shown in Figure 17-b); the trench having similar
dimensions of 100 μm square with a depth of ~3 μm; the square trench is shown without a catalyst patch.

Figure 17: RIE etched trench with Nickel catalyst patch

Trenches were also patterned via KOH etching, which produces sidewalls with a slope of 54.7° to the substrate surface in (100) wafers. An example of a KOH trench with ~15 μm sides and 5 μm depth is shown in Figure 18. Note that this trench has significantly tightened the aspect ratio over the RIE trenches, such that the depth to width ratio goes from 1:50 for the RIE trenches to 1:3 for the KOH trenches. This is not a process limitation, but reflects the progress of designing trenches that better mimic the vertical aspect ratio of CNTs. Further, the KOH trenches were fabricated after the last CNTs were grown at Boston College, so that CNT-bearing pellets with sloping sidewalls were not fabricated.

Figure 18: KOH Etched Trench
4.3.2 Filling & Planarization of Trenches

Pellets are created by spin coating the wafer with the chosen pellet filler material then planarizing the wafer until a smooth, level surface is achieved with the filler isolated into the trenches. Both spin-coating and chemical mechanical polishing (CMP) are done on dies rather than full wafers given the separation into dies during CVD growth. The filler used in our experiments is a two-part epoxy, 610 M-Bond sold by SPI Supplies, and an example of a spun die is shown in Figure 19 below.

![Figure 19: Representative Die with trenches after M-Bond Spin Coating](image)

Note that observation of the die after coating does not indicate any adverse impact on the CNTs, which remain vertically grouped in clusters as grown. Whether this would change for individual CNTs remains to be determined. The thickness of the spun M-Bond is measured on a surface profiler to be approximately 4 μm.

The CMP process exhibits an uneven wear pattern that removes material from the periphery of the die (1-cm square) faster than the center, requiring larger run times to fully planarize an entire die. The time required to planarize a single die is on the order of 1 hour, which is significantly more than initially expected. Further, the process performs better at lower pad pressures and higher spin speeds, with pressure of 5 psi and speeds of 75 rpm having a qualitatively higher material removal rate. A schematic of the gradual planarization of the wafer is shown in Figure 20, showing the shrinkage starting from the

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*This is based on removal and visual observation of the dies every 10 minutes.*
periphery and the trenches forming isolated pellets only after approximately 60 minutes of polishing.

![Figure 20: Schematic of wear pattern of M-Bond during CMP](image)

Macro-scale observation of the die surface shows it to have some curvature, where more of the silicon at the periphery is removed relative to the center. This pattern is similar to micro-dishing known to occur in CMP due to pad flexibility, whereby the pad deforms around the edge of the die, creating a non-planar abrasive surface that wears the edges faster than the center.

At the micro-scale, a contact surface profiler run over a sample of the planarized pellets showed a smooth pellet surface, with a 12 nm step from the pellet surface to the silicon surface, which is not significant. Figure 21 shows SEM images of a silicon wafers with planarized trenches, image (a) shows a top view of the isolated pellets, with a bundle of CNTs in the center, image (b) shows a cross-section of the pellet. The filler material (M-bond) is smooth and even to the surface of the wafer, and is well-isolated into distinct pellets.

![Figure 21: Top view (a) and cross-sectional view of planarized pellets (b)](image)
SEM and AFM examination shows that the CNTs are evenly trimmed by the CMP process, with height variation on the order of a few nanometers. An AFM image of the planarized surface is shown in Figure 22, where the CNTs appear as ring shaped structures (the vertical scale bar on the bottom left has 50 nm increments). The CNTs are all within a few nanometers in length and the major peaks are surface debris, better discerned at lower z-axis sensitivity.

The length uniformity can also be observed by removing the filler material and taking a cross sectional image, as is shown in Figure 23. This figure also shows that there are some CNTs that were sub-length (bright nickel dots slightly lower than overall profile) and therefore not trimmed.
4.3.3 Release of Pellets using XeF₂ Gas Etching

To confirm the selectivity of CNTs to the processes chosen to release the pellets from a silicon substrate as well as for removing the filler material, we tested the effect of oxygen plasma and XeF₂ on CNTs. The results confirm that CNTs are not attacked by oxygen plasma after 30 minutes of exposure, while the M-bond epoxy is removed (e.g. as shown in Figure 23 above). Additionally, the results confirm that XeF₂ does not attack the CNTs while etching silicon, which can be seen in Figure 24, where CNTs remain standing on the etched silicon surface (silicon takes on a wavy, spongy appearance after XeF₂ etching).
These two results, in combination, demonstrate that the processes chosen are compatible with CNTs and are appropriate for use in the nanopelleting fabrication process.

A schematic of the typical XeF₂ etch pattern for pellet release is shown in Figure 25, where the etch gas will isotropically etch the silicon. The pellet filler should not be attacked while the gas etches the silicon from the beneath the pellet perimeter towards its center.

![Figure 25: Typical etch path for XeF₂ gas](image)

Two samples with nanopellets were etched and released, a circular sample (a) and a square sample (b) shown in Figure 26. The etch pattern clearly reflects etching from the periphery to the center, with mound shapes formed in the silicon for circular pellets and pyramidal shapes formed in the silicon for square pellets.

![Figure 26: Released square (a) and circular (b) pellets](image)

An interesting sequence of etch steps over time is shown in the optical microscope images in Figure 27. The images are of circular pellets being released, where the bright areas indicate silicon remains, and the darker areas indicate silicon has been etched. The three images show progress over time, with an etch pattern that seems to indicate some of
the pellets are etched from the outer edges as well as from the center. This is easier to see in image (a) by comparing the center two pellets with those at the left, where the dark dot at the center of the four pellets on the right are the CNTs. For the pellets with CNTs, there is an expansion of the dark area (etching) from both the center and the perimeter, this does not occur for the pellets without CNTs.

![Images of pellets with etching](image_url)

Figure 27: Optical micrographs of XeF$_2$ progress; 4-minutes (a), 8-min. (b), 12-min. (c)

This seems to indicate that there may be some etching through the CNT bundle, either due to XeF$_2$ gas transport through the center of CNTs or at the CNT-pellet interface (the outer interface of the CNT with the pellet filler material). The exact cause of this phenomenon is not known, and it did not occur for all of the round pellets.

SEM imaging of the samples showed that there is a characteristic flattened peak at several of the pellet locations, as shown in Figure 28. This differs slightly from the perimeter-center etching seen in the prior images, and supports perimeter-only etching. This is consistent with the observation that only some of the pellets exhibited perimeter-center etching. One possibility is that the CNTs remain unfilled in their center, and the gas permeates through them. Another potential mechanism is, if there is any amorphous carbon deposited around the multi-walled tube, that the XeF$_2$ etches the amorphous carbon and opens up a channel to the silicon surface. Further study of this phenomenon would be useful to determine the specific causes.
Figure 28: SEM image of XeF₂ exposed silicon after pellet removal

Also of note are the marks on the flat top of the peak, which may reflect the sites from which the CNTs have been uprooted, although this is highly uncertain. The released pellets exhibit good geometrical consistency, and depending on the environment in the XeF₂ chamber, either remain sitting on the silicon substrate or scatter onto the surface of the glass slide supporting the silicon die.

Many of the circular pellets released had CNTs at their center, Figure 29, (a)-(c); oddly, some of the released pellets appeared to have a hole in their center, Figure 29-(d). Such a hole could be related to the CNT bundle in the center being attacked by XeF₂, an appropriate determination of this requires further investigation. Nonetheless, the results for released CNT-bearing pellets demonstrate a proof of concept for pellet creation, and the pellets can then be collected for assembly.
4.4 Additive Process Flow

Creating pellets via an additive process is significantly simpler than etching and planarizing trenches, and this process represents the future trend for this research. The preliminary results for this process are only in the areas of coating and patterning the pellets, which do not have embedded CNTs. Full results with embedded CNTs will be carried out by other researchers once the PE-CVD system under construction is complete.

The first step in creating nanopellets (after patterning CNTs) is to coat the required polymer layers, with the option of applying only an SU-8 coating or a polyimide and SU-8 coating. Both these processes are common microelectronic fabrication processes with well established procedures and widely reported results. We obtain favorable results by using the processing steps described earlier; the more interesting result relates to patterning of the actually layers into pellets.

4.4.1 Single Layer Patterning

Single layer pellets are created by patterning of an SU-8 layer coated onto silicon. Patterning of the SU-8 is carried out by exposing and developing circular patterns on a 120 μm thick layer, which results in posts as shown in Figure 30-(a). The pellets show a bit of taper towards the top, which results from light diffraction effects near the mask-SU8 interface. The pellets adhere fairly well to the surface, but can be broken by mechanical force, as shown in Figure 30-(b) with the stumps remaining on the substrate. Etching such a
sample with XeF₂ would release the pellets cleanly, without a stump forming at the silicon interface. Further, the presence of CNTs at the base of the pellet would impact the failure mechanism due to mechanical force, but should not impact the clean release of the pellets using a XeF₂ etch.

![Figure 30: SU-8 Pellets grown on silicon substrate (a) and lying flat on surface after mechanical felling (b)](image)

4.4.2 Multi-Layer Patterning

Multi-layer pellets are created by coating different polymers and patterning each layer to achieve a post-like pellet with multiple layers. Etching of the SU-8 layer is carried out as before, by exposing and developing to achieve the structure shown in Figure 31. The image shows a cleaved wafer, with a silicon edge (wavy) and a thin polyimide layer with the patterned posts on top.
Patterning of the polyimide layer is carried out by plasma etching as described previously. Figure 32 shows a SEM image of initial attempts to fabricate a bi-layer pellet, after plasma and XeF₂ etching. A 6 µm thick polyimide layer is shown separated from the SU-8 post, which has dimensions of approximately 20 µm x 120 µm. The post has been cleanly separated from the silicon substrate, but the two polymer layers have separated, which is unexpected. Further tests are required to better understand this and develop a more robust process of posts that also contain CNTs.
4.5 Transplanting of Nanopellets

The bridging step between the formation of pellets and their integration into devices is their transplantation. In effect, nanopelleting creates a large number of micro-scale structures that can be assembled using micro assembly techniques. This shift in scale is the key benefit of nanopelleting as a handling method; correspondingly, the targeted technique for transplant is a self-assembly paradigm whereby no operator intervention is required to create the desired structures.

As part of developing the concept, we have utilized an interim assembly solution to position the nanopellets, which is discussed in the first subsection. We have successfully positioned pellets from the additive process into T-shapes (subsection two), and have performed initial attempts at removing the filler material and anchoring CNTs to a new substrate (subsection three). Finally, we have also initially considered the assembly of pellets created using the additive process, which is discussed in subsection four.

4.5.1 Pellet Translation

Manual translation and alignment is carried out on a microprobe station, where 12 μm sharp tips mounted onto x/y/z stages are used to push the pellets into position. The setup used is shown in Figure 33, with the two microprobes converging on a chuck lit by a fiber-optic ring mounted to the microscope head. Movements of the probes are controlled with the knobs shown, and the microscope is linked to a CRT monitor for observation.

![Microprobe station used for pellet alignment](image)
Issues in obtaining good translational and rotational alignment include stiction of the pellets to the probe tip and lack of truly dexterous control over the pellets. An early attempt was made to create a T-shape on a glass slide surface, and this is shown in Figure 34-a). The x-y movements of the probe are visible as trace lines on the glass surface in Figure 34-a). The glass surface provided poor contrast for the optically transparent pellets, which was resolved by placing the slide on a brightly colored surface. Further, the pellets are easily disturbed from their position by vibration of the glass slide in the various manipulation and observation steps. We attempted to resolve this by changing the substrate from glass to silicon and utilizing a low melting point metal as an adhesive layer, which is discussed further in the next section.

![Figure 34: Prior alignment effort (a), and a magnified view of one of the pellets (b)](image)

Another issue with alignment of pellets in our current test samples is sorting of nanopellets that contain CNTs from those that do not. The current samples, as prepared, had CNTs in approximately 40% of the pellets on the die surface, such that a significant quantity of non-CNT-bearing pellets is released alongside those that do contain CNTs (such as that in Figure 34-(b)). This is a result of the initial growth of the metal catalyst patches, which in the initial mask design were only patterned on a portion of the trenches on each die. Ensuring that there are, by design, catalyst patches for all pellets created would resolve these yield issues.
4.5.2 Subtractive Pellet Assembly
We have successfully positioned pellets onto an acceptor wafer surface to form pre-arranged patterns, as shown in the T-shapes in Figure 35. The first pattern is created by aligning pellets manually on a flat acceptor substrate (a); the second pattern by positioning the pellets within a set of acceptor trenches (b) to ease the alignment process. Image (a) shows square pellets aligned onto an Indium-coated substrate, which is heated above its melting point to secure the pellets in place. These square pellets in image (a) do not contain CNTs. For image (b), the circular pellets are pushed into place and dropped into a stable position within the trenches, which are etched slightly larger than the diameter of the pellets (110 μm).

![Figure 35: A T-shape arrangement of nanopellets on an In-coated acceptor wafer surface (a) and a double row of circular pellets in trenches (b)](image)

4.5.3 CNT Anchoring
To image an aligned T-shape composed only of CNT bundles requires the removal of the pellet epoxy material and solidly anchoring CNTs to the acceptor substrate surface. Initial CNT anchoring experiments were conducted with an acceptor substrate having a 50 nm thick evaporated Indium layer. A pellet known to contain CNTs is bonded by placing it on the acceptor wafer surface and heating the wafer to 200°C for 30 minutes. The pellet exhibited fair adhesion to the surface, allowing the wafer to be flipped upside down without displacing the pellet. The bonded pellet is then exposed to oxygen plasma for 30 minutes, removing the pellet material but leaving the CNTs and Indium surface intact. Results of
initial attempts to bond a pellet with a bundle of CNTs to an Indium surface are shown in Figure 36.

Figure 36: Bundle of CNTs (a) before, and after O₂ plasma exposure (b)

Figure 36-b) is taken at an approximate tilt of 25° relative to the wafer normal, and shows the CNTs both standing vertically, leaning, and in some instances possibly lying along the surface. This indicates a mixed result regarding the use of an Indium-based anchoring mechanism.

There are several potential causes for this mixed result, the first is the state of nanotubes embedded within the pellets, the second is the state of the pellet surface, and the third is the ability of Indium to serve as an adhesive base for CNTs. There are several possible states for CNTs embedded with the pellets. Figure 37 shows the three states, sub-length growth that results in CNT variation along the top of the pellet a), perfect growth that results in uniform length along the top and bottom b), and pull-out fracture that results in a break (or complete removal) of the CNT from the bottom side [10]. For either of case a) or c), if the defective side is bonded to the Indium-coated substrate, some of the CNTs will not be anchored. A second consideration for imperfect bonding between the acceptor substrate and the pellet is the condition of the pellet surface.

Figure 37: Possible states for embedded CNTs
Given the pellet processing using CMP, the surfaces is smooth but has some residual particles, as shown in Figure 38. Such particles might interfere with the planar bonding of the pellet to the acceptor substrate, especially if the Indium film is significantly thinner than the size of the debris.

Figure 38: Pellet after CMP and XeF₂ release

A third item of consideration if the compatibility of CNTs and indium in forming an adhesive bond; given a lack of significant literature or prior work on the subject this is not immediately verifiable. Anchoring of CNTs requires further investigation, potentially using built-in anchoring layers or via chemical functionalization of the tubes’ ends.

4.5.4 Additive Process Pellet Assembly
The pellets shown for the subtractive process had aspect ratios of ~ 50:1 in the horizontal dimension, whereas the additive process creates pellets with a aspect ratios of ~ 5:1 in the vertical dimension. This better matches the aspect ratio of vertical CNTs, allows for tighter packing of the pellets and CNTs, and also allows a slightly different assembly mechanism to be used. Rather than pushing flat discs around, as was done previously, interim assembly of the additive pellets is achieved by rolling the pellets across a surface. Preliminary investigation of such an assembly method is carried out in conjunction with another
researcher\textsuperscript{9} in the Micro & Nano System Laboratory, who created v-trenches in a silicon surface and positioned the pellets into them, and example of which is shown in Figure 39.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure39.png}
\caption{Post-shaped pellet rolled into V-trench}
\end{figure}

\textsuperscript{9} Dr. Y.-A. Song, who is also the source of this image.
5.0 Discussion & Future Work

The results presented in the previous chapters presented the challenges for CNT growth, the potential benefits of the nanopelleting concept, and favorable preliminary experimental results to support the concept. Specifically, we have demonstrated that pellets with embedded CNTs can be formed with uniform geometry, selectively released from the substrate, and transplanted and positioned on an acceptor substrate. This opens up the opportunity of using this method to harvest nanopellets and reassemble them in large scale onto acceptor substrates, creating CNT-based devices that could not otherwise be reliably made.

There are several areas in particular that require further work to develop and refine this technique. These include the development of pellets with individual carbon nanotubes, further development of the additive process, in particular multi-layer pellets, and third the development of reliable self-assembly methods to complement nanopelleting. These are discussed in the next three sections. Also of interest for future consideration are potential applications for nanopellets, not just CNTs, but of applications that are enabled by or compatible with nanopelleting. Such potential applications are discussed in section four. Finally, a recapitulation concludes the thesis by summarizing the major concept and results.

5.1 Individual CNT Pellets

The ultimate nanopellet would contain a single CNT, allowing for added flexibility in developing applications and taking advantage of the sizing of the CNT. The results to date have demonstrated creation of pellets with CNT bundles, but future work should aim to integrate individual CNTs into pellets. The growth of individual CNTs by CVD has been demonstrated by other researchers, and this result should be straightforward to replicate once the CVD chamber under construction is complete. The two difficulties in integrating individual CNTs into nanopellets are 1) the creation of sub-micrometer catalyst patches with high throughput and at low cost, and 2) the potential difficulties in casting polymers without disturbing individual CNTs.
So far the catalyst patches used in CVD growth have been in the micrometer size range, which causes bundles of CNTs to grow. Using the e-beam patterning of sub-micrometer patches demonstrated in the results, and the CVD chamber under construction at MIT, growing individual pellets should be straightforward. To develop the process for larger-scale commercialization, a parallel patterning technique for sub-micrometer catalyst patches would be useful. Two technologies in particular are promising for this purpose, x-ray lithography that utilizes a hard mask to expose wafer surfaces in a similar overall manner to optical systems but replacing UV rays with x-rays. The second technology, Zone Plate Array Lithography, developed at the Nano Structures Laboratory at MIT, utilizes arrays of lenses focusing switched light beams to pattern sub-micrometer features without a mask. The throughput of both techniques is not as high as optical lithography, but in the long term should allow for improved processing speed at lower cost compared to e-beam lithography.

The results of casting polymers around vertically standing CNT bundles have favorably supported the compatibility of this technique with CNTs. The tubes are not disturbed from their vertical position and the polymer does fill the volume around the CNTs (wetting). An individual vertically-aligned CNT may behave similarly, although without the support of surrounding tubes may deflect somewhat. Future studies should provide an answer to this issue. With regards to wetting and casting, the individual CNT should, if anything, be easier to embed. Should alignment stability be an issue for individual CNTs future studies may investigate the use of vapor coating the CNT (e.g. with parylene-C) to initially fix the CNT and then cast the polymer as before.

5.2 Additive Processing & Multi-layer Pellets
The initial results from the additive process flow are interesting for several reasons. First, the geometry of the pellets is significantly improved such that the pellets have aspect ratios more inline with those of CNTs. Second, the processing is simplified by reducing several time consuming steps. Third, the technique offers the capacity to make multi-layer pellets that enable control over the CNTs’ relationship to the pellet. A potential downside to this process, given that it eliminates the CMP trimming step, is the lack of precise length control;
the importance of this depends on the application and should length be an issue the subtractive process remains a viable option.

Of particular interest for future work is the capability to create pellets with multiple layers. By creating layers of precise thickness and then removing them selectively, a controllable portion of an embedded CNT can be exposed, creating structures resembling candles, as shown in schematic form in Figure 40.

![Figure 40: Multi-Layer Pellets - "Nanocandles"](image)

The schematic shows a multi-layer pellet with an embedded CNT that is then released from the substrate and then one of the layers is removed. The relative height of the CNT and each layer thickness can be controlled, offering reliable geometrical control over the exposed CNT tip. We demonstrated the growth and patterning of two layers, and future work should aim to integrate individual CNTs as well as CNT bundles into such structures. Also of potential merit would be attempts to create pellets with three layers, allowing the CNT to be exposed on both sides, with the remaining layer serving as a gripper for mechanical manipulation.

5.3 Pellet Transplant & Assembly

The key step for future work to develop nanopelleting into a commercially viable manufacturing method is to combine its features with a robust assembly method. We have demonstrated initial transplant and positioning using manual methods, but to enable the development of large-scale devices a faster, simpler assembly technique is necessary. There are several promising techniques for this, particularly fluidic self-assembly techniques similar to those reviewed in chapter two.

Such techniques would require the either a particular geometry for the pellets or the coating of one side of the pellets with a self-assembling monolayer. For subtractive processing, pellets with sloping sidewalls could be created and assembled onto similar
acceptor substrates, as demonstrated by Alien Technologies’ Fluidic Self Assembly. In this technique microblocks (which they call nanoblocks) are suspended in solution, and then are flowed over a substrate with corresponding patterns to the blocks, such that they settle into a stable mating configuration. The development of KOH etched trenches to fabricate pellets and receptor sites would then mimic the basic parameters of this technique. Given the proprietary and patented nature of this method, however, collaboration with Alien Technologies might be a potentially more feasible route for developing this assembly route.

For additive processing, the straight angles and high aspect ratios could be compatible with either vertical or horizontal assembly techniques. That is, pellets could either be positioned to stand upright orthogonal to a surface, or rolled into place to lay parallel to a surface. For vertical assembly, a fluidic self-assembly technique similar to that of Srinivasan et al. [52] at UC Berkeley is a useful starting point for further work in this area. Potential horizontal self-assembly techniques include the use of Langmuir Blodgett techniques for fluidic assembly, although this technique would require comparatively more development to be adapted to nanopelleting.

Srinivasan et al.’s technique utilizes capillary forces between two hydrophobic surfaces patterned onto the microstructure and the substrate. To create the hydrophobic binding sites, matching gold films are patterned on both parts and self-assembled monolayers of alkanethiol precursors are patterned on the gold. The microstructures are suspended in a solution, and the substrate is passed through a liquid hydrophobic adhesive film, such that the microstructures adhere to the substrate binding sites and not each other. To replicate this technique, hydrophobic patterns would need to be created on one side of the pellets, which would then be suspended in solution and adhered to substrates in the same manner as the system described. This technique would require some additional steps in the process plan, but is promising for large-scale self-assembly of nanopellets.

5.4 Applications
Applications that are particularly well suited to nanopelleting are those that require large expanses of arrayed CNTs with specific geometries, alignment and location. Examples of such applications include field emission systems for display technology, where even a
relatively small display of several square inches would require vast numbers of ordered CNTs. Such large-scale fabrication is simplified via nanopelleting’s growth, harvesting, and assembly pathway. Moreover, by allowing the use of micro-scale self-assembly techniques, nanopellets provides for deterministic control over CNT location and orientation for device fabrication.

Other potential applications that may be enabled by this technique but are yet underexplored include the use of CNT arrays for image patterning using either thermal energy or electron beams. By creating arrays of CNTs on substrates, and then linking the array to an addressable energy source, switched energy transmission through the CNTs would be possible. Such a system could then be used to selectively pattern resist films without a traditional mask.

Yet other potential applications include structural applications such as carbon fiber composite interconnects. Moreover, given the broader utility of the nanopelleting concept in terms of multi-scale system design, nanopelleting can be used more broadly as a handling method for a variety of nanostructures and their applications. Potential applications should develop once the concept matures into a developed technology and other researchers also utilize the concept in developing applications.

5.5 Recapitulation
This thesis has taken the nanopelleting concept from its vague initial stages, developed specific process plans for fabricating nanopellets, and shown the experimental setup and results for first generation nanopellets. The results support the merit of nanopelleting as a means of controlling nanostructures, specifically CNTs. In particular, the harvesting of nanopellets allows for development of applications with large-scale assemblies of CNTs. The technique represents an efficient method for growing and handling of CNTs. Further work to optimize the design, link it with assembly techniques, and develop related applications would be useful.
Bibliography


