Chapter X

Principles and Methods for Integration of Carbon Nanotubes in Miniaturized Systems

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Abstract:
The outstanding properties of carbon nanotubes (CNTs) make them a compelling material for use in applications including nanoscale circuits, flexible conductors, battery electrodes, and reinforced composites; and their combination of attractive mechanical, thermal and electrical properties makes CNTs truly unique. However, as with any new material, practical use of CNTs requires efficient and scalable processing methods, and commercial development requires these methods to be compatible with existing manufacturing platforms such as semiconductor processing. This chapter presents a thorough review of methods for integrating CNTs in micro- and nano-devices and systems, focusing on challenges of: controlling CNT size and structure; precisely placing and packing CNTs; and achieving device-compatible growth and processing methods. Examples are selected across the spectrum from early-stage research to present commercialization. Overall, while we are far from meeting the aforementioned challenges, near-term uses of CNTs will include interconnects, non-volatile memory, inertial sensors, and thermal interfaces.

1. The promises and challenges of carbon nanotubes

As seamless cylinders of carbon atoms arranged in a hexagonal lattice, carbon nanotubes (CNTs) are the third allotropic form of carbon in addition to diamond and graphite (Dresselhaus & Avouris, 2001). The nature of CNTs as long continuous molecules imparts exceptional material properties, including several times the strength of steel piano wire at one-fifth the density, at least five times the thermal conductivity of copper, and high electrical conductivity and current-carrying capacity (Dresselhaus et al., 2001; Rotkin & Subramoney, 2005). Incidentally, while research and development in science and applications of CNTs has boomed during the past 15 years, filamentous carbon has been studied and used for over a century. Many researchers unknowingly worked with CNTs well before the atomic structure of a CNT was first observed by Sumio Iijima of NEC.

The exceptional properties of CNTs, along with application-oriented characteristics (Baughman et al., 2002; Endo et al., 2004; Endo et al., 2006) such as high surface area, diverse capabilities for chemical modification and functionalization, and strong interactions with polymers and composite host materials, create many possible opportunities for their use in next-generation micro- and nano-devices and systems (“N/MEMS devices”). However, as with any new material or process, many challenges exist in making CNTs compatible with the existing microfabrication processes that have shouldered the microelectronics and MEMS industries.

To frame the content of this chapter, we identify 5 major challenges for the integration of CNTs in N/MEMS devices:

1. Controlling the chirality, wall number, and defect density of individual CNTs during synthesis, or via post-synthesis processing.
2. Achieving precise and directed placement of individual CNTs or CNT bundles in a repeatable fashion over large areas.
3. Controlling the orientation and packing of CNTs into dense assemblies, such as in vertical pillars or lateral films.
4. Establishing low-resistance (e.g., electrical, thermal) contact to CNTs as well as strong interconnection among CNTs and with supporting materials.
5. Achieving compatibility of growth and/or deposition of CNTs with device fabrication processes (typically lithography).

This chapter will address: (1) the structure and properties of CNTs; (2) methods of CNT synthesis by chemical vapor deposition; (3) methods of integrating CNTs into N/MEMS devices; and (4) selected examples of devices that utilize CNTs for electrical, mechanical, electromechanical, and thermal functions.

2. The structure and properties of CNTs

2.1 CNT Structure

CNTs are distinguished by their number of concentric layers (with spacing 0.34 nm), and their chirality. The most distinct CNT structures in terms of numbers of walls are single-wall CNTs (SWNTs), double-wall CNTs (DWNTs), and multi-wall CNTs (MWNTs), which are illustrated in Fig. 1. Typically, SWNTs are 0.4–5 nm in diameter, and MWNTs are up to 100 nm in diameter. Further, many interesting supramolecular constructs have been demonstrated, such CNTs packed with fullerenes (C_{60}); these are called “peapods” (Smith et al., 1998).

If we visualize the formation of a CNT as the action of rolling a graphene sheet into a seamless cylinder, the chirality of a CNT is established by the orientation of the graphene lattice with respect to the axis of rolling. The chirality is denoted by (n,m) indices (Fig. 2) according to a convention introduced by Dresselhaus (Dresselhaus et al., 1995; Dresselhaus
et al., 2001). The chirality determines the band gap, and therefore the electronic properties of a CNT. For example, “armchair” SWNTs, which have a straight edge of the hexagonal lattice perpendicular to the tube axis, have a small band gap and are typically metallic. Conversely, “zigzag” SWNTs, which have a straight edge of the hexagonal lattice parallel to the tube axis, are metallic in one-third of cases and semiconducting in two-thirds of cases. The band gap of a CNT is inversely proportional to the tube diameter. All CNTs larger than approximately 3 nm in diameter have band gap energies less than the thermal energy at room temperature, and therefore exhibit metallic behavior. Hence, while SWNTs can be semiconducting or metallic, MWNTs are almost always metallic. Overall, there are hundreds of possible CNT structures having different diameter and chirality pairings. Geometric and energetic calculations suggest that the pentagon/hexagon arrangement of the cap uniquely determines the chirality of a SWNT (Reich et al., 2005).

Figure 1. a) CNT structures: (from left to right) single-wall CNT (SWNT), multi-wall CNT (MWNT), double-wall CNT (DWNT), and SWNT “peapod” (adapted from (Dresselhaus et al., 2003)). b) TEM: (from left to right) of a SWNT, MWNT, and SWNT “peapod” (adapted from (Iijima, 1991; Zhong et al., 2009; Koshino et al., 2010)).
Figure 2. a) Chiral orientations of CNTs, represented by the alignment of the CNT axis with particular lattice points of the graphene sheet, which determine the \((n,m)\) index of the CNT (from (Dresselhaus et al., 1995))  b) Visualization of SWNT structure by wrapping of a graphene sheet (from (Wikipedia & Arnero, 2007)).
2.2 CNT Properties

Table 1 below summarizes the electrical, mechanical and thermal properties of CNTs and various other materials including gold and silicon which are widely used in N/MEMS. In the following subsections, we discuss the electrical, mechanical, thermal, and fluidic properties of CNTs.

Table 1. Mechanical, thermal and electrical properties of CNTs, CNT fibers (CNTFs), carbon fibers (CFs), and various other materials (\(E =\) Stiffness, \(S =\) Tensile Strength, \(\rho =\) Density, \(E/\rho =\) Specific Stiffness, \(\sigma/\rho =\) Specific Strength, \(k =\) Thermal Conductivity, \(\sigma =\) Electrical Conductivity. The listed values of specific strength and specific stiffness are normalized relative to those of steel. Properties of metals were obtained from (Matweb, 2010). Properties of carbon and synthetic fibers are as listed in (NAS, 2005). Thermal conductivities of polymer and CNT fibers are generally much less than for carbon fibers.

<table>
<thead>
<tr>
<th>Material</th>
<th>(E) [GPa]</th>
<th>(S) [GPa]</th>
<th>(\rho) [g/cm(^3)]</th>
<th>(E/\rho)</th>
<th>(\sigma/\rho)</th>
<th>(k) [W/m-K]</th>
<th>(\sigma) [S/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT(^a)</td>
<td>1000</td>
<td>20-200</td>
<td>1.4</td>
<td>28</td>
<td>60-1100</td>
<td>&gt;3000</td>
<td>1x10(^{11})</td>
</tr>
<tr>
<td>PAN/Pitch CF(^b)</td>
<td>500</td>
<td>4</td>
<td>1.8</td>
<td>11</td>
<td>19</td>
<td>500</td>
<td>-</td>
</tr>
<tr>
<td>CVD-spun CNTF(^c)</td>
<td>15</td>
<td>1.0</td>
<td>2</td>
<td>0.3</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dry-spun CNTF(^d)</td>
<td>15</td>
<td>0.3</td>
<td>0.8</td>
<td>0.7</td>
<td>3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Polymer-CNTF</td>
<td>100</td>
<td>0.9</td>
<td>1.5</td>
<td>2.6</td>
<td>4.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Glass fiber</td>
<td>74</td>
<td>3.5</td>
<td>2.6</td>
<td>1.1</td>
<td>11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Kevlar</td>
<td>87</td>
<td>3.0</td>
<td>1.4</td>
<td>2.3</td>
<td>16</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M5 fiber</td>
<td>375</td>
<td>7.6</td>
<td>1.7</td>
<td>9</td>
<td>35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Steel (1080)</td>
<td>205</td>
<td>1</td>
<td>8</td>
<td>1</td>
<td>1</td>
<td>48</td>
<td>5.6x10(^{6})</td>
</tr>
<tr>
<td>Al (6061)</td>
<td>69</td>
<td>0.3</td>
<td>3</td>
<td>1.0</td>
<td>0.9</td>
<td>170</td>
<td>3.7x10(^{7})</td>
</tr>
<tr>
<td>Ti (8Al-1Mo-1V)</td>
<td>120</td>
<td>0.9</td>
<td>4</td>
<td>1.1</td>
<td>1.6</td>
<td>6</td>
<td>1.8x10(^{8})</td>
</tr>
<tr>
<td>Cu (UNSC10100)</td>
<td>115</td>
<td>0.4</td>
<td>9</td>
<td>0.5</td>
<td>0.3</td>
<td>380</td>
<td>5.9x10(^{7})</td>
</tr>
<tr>
<td>Si</td>
<td>112</td>
<td>7(^e)</td>
<td>2.3</td>
<td>1.9</td>
<td>24</td>
<td>149</td>
<td>10(^{-3})</td>
</tr>
<tr>
<td>Au</td>
<td>77</td>
<td>0.1</td>
<td>19.3</td>
<td>0.2</td>
<td>0.05</td>
<td>301</td>
<td>4.5x10(^{8})</td>
</tr>
</tbody>
</table>

\(^a\) (Krishnan et al., 1998; Kim et al., 2001; Barber et al., 2005; Li et al., 2005)
\(^b\) (Li et al., 2004; Motta et al., 2005)
\(^c\) (Zhang et al., 2004)
\(^d\) (Dalton et al., 2004; Ericson et al., 2004)
\(^e\) (Madou, 2002)
2.2.1 Electrical Properties

Interest in the electrical characteristics of CNTs is largely because the semiconducting character of SWNTs makes them useful in transistors and other circuit elements, and because CNTs can exhibit very high electrical conductivity due to their small dimensions and high structural quality. In particular, room-temperature ballistic electron transport has been demonstrated over μm-scale distances in SWNTs (Javey et al., 2003; Wind et al., 2003) and multichannel MWNTs (Li et al., 2005). Under these conditions, the electrical conductivity of CNTs exceeds that of copper.

These attributes—chirality-dependent band gap, and low-resistance transport—make SWNTs more frequently studied for use in next-generation transistor devices (Tans et al., 1998; Javey et al., 2003; Chen et al., 2006), and MWNTs are sought for their high conductivity due to their metallic character. Further, while individual CNTs have been studied widely for their electronic properties as active device elements, a larger-scale and nearer-term opportunity exists for assemblies of CNTs to replace copper (Cu) in vertical and horizontal electronic interconnects, at both local and global chip-scale dimensions (Peercy, 2000; ITRS, 2007). At emerging linewidths (~20-40nm and below), Cu will be unsuitable for interconnects due to electromigration and boundary scattering; however, CNTs are resistant to electromigration, have μm-scale electron mean free path (Javey et al., 2003; Li et al., 2005), and withstand higher current densities (10⁹ A/cm² vs. 10⁷ A/cm²) than Cu (Naemi et al., 2005; Naemi & Meindl, 2007). Calculations also suggest CNTs can decrease switching energy consumption, and GHz operation of individual and bundled CNTs as a horizontal interconnects has been demonstrated (Close et al., 2008; Tselev et al., 2008).

Importantly, assemblies of CNTs exhibit much lower values of electrical conductivity than predicted by linear scaling of the properties of individual CNTs, as shown in Figure 3. Such shortfalls are due to structural defects inherent in as-grown CNTs and non-uniform and non-ideal metal contacts that do not necessarily address all walls of every CNT. Further, in isotropic networks such as tangled CNT films, CNT–CNT junction resistances can far exceed the bulk resistance of CNTs over short distances. In this regard, continuous, aligned CNTs compose an ideal network morphology that does not suffer from such CNT–CNT resistances.

Making low-resistance electrical contact to CNTs has been a practical challenge, and relies on intimate engagement between the metal and the conduction path through the CNT. Ohmic contact to metallic CNTs was first achieved by deposition and subsequent annealing of gold electrodes (Soh et al., 1999), and later it was found that Pd-CNT interfaces do not exhibit Schottky barriers and thereby enable observation of ballistic transport in semiconducting tubes (Javey et al., 2003). Integration of parallel, electrically contacted CNTs could be improved by plasma etching to open their ends (Zhu et al., 2006), as has been demonstrated through room-temperature superconductivity measurements of MWNTs having ends rooted in Au (Takesue et al., 2006).
Figure 3. Previously published calculations of electrical conductivity along continuous CNTs as related to the CNT packing fraction, compared to previously measured electrical data for individual CNTs and CNT networks. The packing fraction is defined as the ratio of the CNT areal density (number of CNTs/cm²) to the areal density of hexagonally packed CNTs (modeled as cylinders) having the same outer diameter. Solid and dashed X marks are MWNTs and SWNTs, respectively. We assume that the conductivity of an aligned CNT network is linearly proportional to the number of CNTs per unit cross-sectional area and that the constant of proportionality is the conductivity of an individual CNT (Fischer et al., 2003; Li et al., 2005).

2.2.2 Mechanical Properties
The density-normalized mechanical stiffness and strength of CNTs exceed those of all known natural and synthetic bulk materials (Table 1). As a CNT is conceptually a rolled sheet of graphene, its tensile elastic modulus is closely approximated by the in-plane
modulus of single crystal graphite, which is \( \approx 1000 \text{ GPa} \). Theoretically, this value is independent of the CNT diameter, except for a slight decrease due to curvature effects in very narrow SWNTs (Dresselhaus et al., 2003), and this has been confirmed by a wide body of experimental work.

Theory predicts that the ultimate tensile strength of a material is approximately one-tenth of its elastic modulus, or \( \approx 100 \text{ GPa} \) for small-diameter CNTs; however, the inevitable presence of defects (i.e., vacancies, Stone-Wales transformations) prevents this limit from being realized. Testing of CVD-grown MWNTs gave a tensile strength distribution (by Weibull statistics), where 25% of the CNTs fail at or below 55 GPa, and 75% of the CNTs fail at or below 148 GPa (Barber et al., 2005). Further experiments have strained SWNTs to \( \approx 6\% \) elongation before breakage (Walters et al., 1999). Superplastic elongation to strains exceeding 250% has been demonstrated by pulling a SWNT in a TEM while resistively heating it to above 2000 °C (Huang et al., 2006).

Beyond individual CNT devices, the prospects for scaling the mechanical properties of CNTs into larger assemblies require effective management of the interconnections between CNTs, and engineering of composite materials that bind CNTs to matrix materials. Composite microstructures containing CNTs could significantly enhance micromechanical material properties, which could be tuned by the packing fraction of CNTs within the matrix (Ashrafi et al., 2006). Encouragingly, pull-out tests have measured CNT-polymer adhesion strength exceeding 100 MPa (Cooper et al., 2002; Barber et al., 2003), suggesting that \( \mu \text{m} \)-length contact between CNTs and polymers can effectively impart the native strength and stiffness of CNTs to a composite microstructure.

### 2.2.3 Thermal Properties

Along with their outstanding electrical and mechanical characteristics, high-quality CNTs have thermal conductivity exceeding the in-plane thermal conductivity of graphite (Hone, 2001). The room-temperature thermal conductivity of an individual suspended SWNT has been measured to be 3500 W/m·K (Pop et al., 2006), and ballistic phonon transport through MWNTs has been experimentally verified (Chiu et al., 2005). As a result, CNTs are a promising choice among additives for high thermal conductivity fluids and thermal interface materials (TIMs) for thermal management applications. Exceptional improvement of 150% in effective thermal conductivity of oil was achieved with only 1 vol % of CNTs suspended in oil (Choi et al., 2001). 125% improvement in thermal conductivity of epoxy was also achieved with 1 wt % of CNTs added (Biercuk et al., 2002).

Even higher thermal conductivity may be achieved using organized (e.g., aligned) CNT assemblies; however, as has been observed for electrical properties, assemblies of CNTs typically have lower thermal conductivities than a single CNT. For example, a magnetically aligned array of SWNTs was measured to have thermal conductivity of 200 W/m·K (Hone et al., 2000). Packing fraction plays a big role in determining the final thermal conductivity of the assembly, as is the case with electrical and mechanical properties. Also, the orientation of the tube within the assembly, inter tube junctions, presence of defects on individual tubes all drive down the bulk thermal conductivity of a given assembly. For 100-nm diameter MWNTs, an assembly of randomly oriented CNTs has thermal conductivity of 0.17 W/m·K (Prasher et al., 2009), whereas an assembly of VA-CNTs has thermal conductivity of 15 W/m-
K (Yang et al., 2002), which is almost a 100 fold difference. This discrepancy is due to phonon scattering at tube-tube contacts, once again highlighting the importance of organizing and interconnecting CNTs to achieve favorable scaling of individual CNT properties.

2.2.4 Fluidic Properties

A fourth and final attractive attribute of CNTs is their ability to confine materials and transport fluids in their inner cavity. Since initial TEM observation of capillary uptake of liquid metals into CNTs (Ajayan & Iijima, 1993), it has been known that CNTs could be used as nanofluidic “pipes”. Recently, CNT membranes were made by infiltrating a CNT forest with a polymer or ceramic matrix, and opening the CNT ends to facilitate flow through the CNTs (Hinds et al., 2004; Holt et al., 2004). Experiment and theory shows that gases and liquids flow through CNTs with very high slip; for example, owing to the smoothness and hydrophobicity of CNT walls, water and organic solvents flow through multi-wall CNTs (7nm ID) at rates 10^4–10^5 times continuum predictions (Majumder et al., 2005). Double-wall CNTs (1.5nm ID) exhibit mass-dependent selectivity of gas flows (Holt et al., 2006) and functional groups on the ends of the tubes facilitate ion exclusion from liquids at concentrations where the Debye length is larger than the CNT diameter (Fornasiero et al., 2008). Further, CNTs respond electrically to the chemistry, rate, and direction of flow by mechanisms of potential ratcheting (Ghosh et al., 2003; Sood & Ghosh, 2004), collision-induced resistivity (Romero et al., 2005), and charge donation (Snow et al., 2006).

3. CNT Synthesis by Chemical Vapor Deposition

Since the mid 1990’s, catalytic chemical vapor deposition (CCVD or CVD) has emerged as the most versatile and scalable method of CNT synthesis, owing to its low reaction temperatures (relative to arc, laser, and flame methods), high yield, and versatility for gas-phase (“floating catalyst”) or substrate-bound (“fixed catalyst”) growth (Dai, 2001; Teo et al., 2004; Terranova et al., 2006). Iijima’s 1991 study found CNTs in the deposit on the carbon electrode of a DC electric arc (Iijima, 1991); this apparatus was very similar to that reported for synthesis of large quantities of C60 fullerenes (Kratschmer et al., 1990). CNTs can also be produced in flames (Howard et al., 1991; Goel et al., 2002; Height et al., 2004), by laser ablation of carbon (Thess et al., 1996), by direct conversion of carbon using microwave energy (Yoon et al., 2006), and by many occasional procedures which are too numerous to mention. In concert with the focus of integration with micro/nanofabrication, this section addresses CVD methods in detail.

In the CVD process, CNTs form by organization of carbon on a nanoscale metal catalyst particle in a high-temperature carbon-containing atmosphere (Fig. 4a). The carbon dissociates from the source compound and adds to the CNT through surface and/or bulk diffusion at the catalyst. The catalyst particle can remain rooted on the substrate during CNT growth (“base growth”), or can lift from the substrate and remain at the tip of the advancing CNT (“tip growth”). In both cases, carbon is added at the catalyst site. The growth kinetics, catalyst-substrate surface interactions, and forces acting on the catalyst particle (e.g., forces induced by an electric field in plasma-enhanced CVD (Merkulov et al., 2001) determine whether base growth or tip growth occurs (Melechko et al., 2002).
A highly simplified picture of CNT by CVD can be gained via an analogy to the vapor-liquid-solid (VLS) crystal growth, which was first studied during the 1960’s for growth of silicon whiskers (Wagner & Ellis, 1965). In the VLS model, a vapor-phase precursor dissolves into a liquid growth site (catalyst), and a solid crystal precipitates from the growth site. CNT growth from metal can be described by the VLS model as a high-level example; however, under certain circumstances (e.g., at high temperature and if the catalyst is liquefied) carbon may diffuse through the bulk of the catalyst, while under other conditions (e.g., at lower temperature) surface diffusion may dominate (Snoeck et al., 1997; Ding et al., 2005; Hofmann et al., 2005). Growth from many catalysts, including oxides, also complicates the applicability of the VLS model to CNT growth. The VLS mechanism is more directly applicable to growth of semiconductor nanowires (Wu & Yang, 2001), such as silicon nanowires which precipitate from gold nanoparticle catalysts in a silane (SiH₄) atmosphere (Cui et al., 2001; Kodambaka et al., 2006).

CVD growth of CNTs can be performed in a variety of closed-atmosphere furnace apparatuses, in which pressure, temperature, and gas flow are controlled (Fig. 4b). These apparatuses are typically suited to either “fixed-catalyst” (substrate-bound) CNT growth, where the CNTs grow from catalyst particles arranged on a substrate such as a silicon wafer, or to “floating-catalyst” growth where the catalyst particles are held in a fluidized bed or pass through the furnace continuously in the gas phase.

In substrate-bound growth, control of the density and placement of the catalyst particles on the substrate, and application of external forces (e.g., gas flows, electric fields, mechanical obstructions) can be used to engineer the orientation and packing of CNTs during growth. As shown in Fig. 5, four exemplary CNT configurations have been found: (1) tangled CNT films which resemble nanoscale spaghetti; (2) isolated CNTs which can be grown across microfabricated bridges, or suspended in gas flows to reach millimeter or longer lengths (Huang et al., 2003; Zheng et al., 2004); (3) horizontally aligned CNTs grown due to directional interactions with single-crystal substrates such as quartz and sapphire; (4) and vertically aligned CNT “forests” that grow perpendicular to the substrate. While isolated SWNTs can be grown to millimeter- or centimeter-lengths when suspended during growth by a gas flow; however, the density of catalytic sites must be very low to prevent entanglement among CNTs because the CNTs will flutter in the gas flow. At a high catalyst density and CNT growth rate, the CNT forest growth mode is typical whereby the CNTs self-orient perpendicular to the substrate surface due to initial crowding and continue to grow upward in this direction (Terrones et al., 1997; Fan et al., 1999).
Figure 4. Schematics of individual substrate-bound CNTs growing by CVD: (a) “base growth” of a CNT, where a gaseous carbon source diffuses at a metal catalyst particle which remains attached to the substrate, and a CNT grows upward from the surface of the particle; (b) base and tip-growth of CNTs rooted in a nanoporous (e.g., zeolite) substrate (from Hayashi et al., 2003)). Classical furnace designs for CVD synthesis of CNTs and like nanostructures (from Teo et al., 2004)): (c) horizontal tube furnace with fixed catalyst (d) low pressure plasma-enhanced (PECVD) chamber with heated stage.
Figure 5. Classical morphologies of CNTs grown on substrates: a) tangled film, which terminates at \(~\mu m\) thickness due to steric hindrance among CNTs (image from (Hart et al., 2006)). b) vertically-aligned film, which can grow uniformly to \(~\mu m\) thickness (image from www.nanobama.com). c) a single CNT suspended over microfabricated channels (image from (Jungen et al., 2007b)). d) horizontally-aligned CNTs on the substrate (image from (Kocabas et al., 2005)).

CNT growth by CVD involves many process parameters, and therefore a multi-dimensional parameter space must be explored to develop an empirical model of a particular growth scheme, and to relate the characteristics of the CNTs to the process conditions. CNT characteristics of interest include diameter, wall structure and chirality, defect density, and length, as well as the many physical properties which result from these basic characteristics.
4. Methods of CNT integration in N/MEMS

This section reviews emerging methods to integrate CNTs in N/MEMS. We aim to present how CNTs can be interfaced with device substrates and in functional configurations, so the CNTs can be connected mechanically and/or addressed with electrical contacts.

4.1 Device-compatible CNT growth methods

Perhaps the most straightforward approach for integrating CNTs into small devices is to synthesize them directly on-chip. This offers advantages in scalability for industrial processes, since it relies mainly on photolithography and other standard microfabrication methods for defining the catalyst. However, it is challenging to synthesize high-quality CNTs on electrically conductive substrates at temperatures compatible with complementary metal-oxide-semiconductor (CMOS) processing, which are typically limited to 450 °C (Awano et al., 2006; Nessim et al., 2009). Further, repeatable and uniform growth needs to be achieved over 200 or 300 mm wafers for the processes to be relevant for industry. While CNTs must be connected to conductive substrates for active sensing and actuation applications, they can also be connected merely to insulative substrates (e.g., oxides) if only passive functionalities are required (such as for springs to support suspended microstructures or passive absorbents for detection/analysis). In the latter case, growth in device configurations is easier because oxides typically tolerate higher processing temperatures than metals.

Nevertheless, the temperature limitation remains an obstacle for achieving high-quality CNTs on-chip, especially ensembles of vertically aligned CNT forests, which require a high number density (10^9-10^12 cm^-2) in order to self-orient during the synthesis process. Successful CNT growth depends both on effective decomposition and rearrangement of the hydrocarbon precursor and formation of stable catalyst nanoparticles, which facilitate deposition of carbon and incorporation into the existing CNT lattice structure. Low-temperature growth is especially challenging because the decomposition temperature of most hydrocarbons used for CNT growth well exceeds 500 °C. However, high temperatures often lead to alloying between catalysts and metallic underlayers, which often hinders CNT growth (Nessim et al., 2010). To meet this need, plasma-enhanced CVD has been used widely to achieve low-temperature CNT formation, in which the plasma source provides the energy needed to generate active hydrocarbon species for CNT growth (Chhowalla et al., 2001; Zhong et al., 2005). However, plasma-enhanced methods can also generate undesirable defects in the CNT structure, presumably due to etching by ionized species or radicals (Ren et al., 1998; Lee et al., 2009). Recent progress in chemically engineering CNT growth has enabled synthesis temperatures below 400 °C by an oxidative dehydrogenation method (Magrez et al., 2010); however, more investigation is required in order to reveal the utility and suitability of this process for small devices.

Alternatively, thermal treatment of the feedstock gases prior to reaching the catalyst substrate (i.e., “preheating”) has been shown to enhance CNT growth for samples with catalysts on both electrically insulating substrates (Lee et al., 2001; Jeong et al., 2002; Mora et al., 2008; Meshot et al., 2009) and conducting (metallic) substrates (Awano et al., 2006; Nessim et al., 2009). Decoupling gas pretreatment from the catalyst temperature, as shown in Fig. 6a, allows synthesis at low substrate temperatures without sacrificing control of the
gas chemistry. Gas analyses have shown that diverse hydrocarbons, including volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs), are formed by thermal treatment of typical feedstock gases (Meshot et al., 2009; Plata et al., 2009). This understanding of the growth ambient has been used to engineer the synthesis process to not only tune the diameter and quality of the CNTs but also their growth kinetics for rapid (>10 µm/s) growth to millimeter lengths (Meshot et al., 2009). Further, the decoupled CVD method has enabled tunable transformations from fiber-like carbon structures to crystalline CNTs (Fig. 6b), having far more desirable electrical properties (Nessim et al., Submitted for publication.).

Figure 6. a) Schematic of a custom-built, atmospheric-pressure CVD apparatus (SabreTube, Absolute Nano), which features local Joule heating of a Si platform to independently control the catalyst temperature $T_s$ from the preheated feedstock gases (at $T_p$). A laser displacement sensor mounts on the outside of the growth chamber and measures real-time kinetics of the growth process (Meshot & Hart, 2008). b) TEM images of carbon structures synthesized at $T_s = 525 \, ^\circ\text{C}$ for various $T_p$ values. We observe a distinct evolution from amorphous structures to CNTs with crystalline walls as $T_p$ increases (Nessim, et al.).
4.2 Methods of integrating individual CNTs in devices
In this section, we will look into methods to integrate a single, isolated SWCNT or MWCNT in device-relevant configurations. Four exemplary approaches have been pursued so far; the first three use CNTs which are grown separately from the device, and the fourth approach places isolated CNTs by direct growth in the device.

- **Alignment of microsystems around randomly dispersed CNTs.** One of the first methods developed to integrate isolated CNTs in MEMS is to deposit them from a solution, resulting in randomly arranged CNTs on a substrate. After the deposition, e-beam lithography is used to define microstructures on or around the individual CNTs (Stampfer et al., 2006a). Alternatively, electrodes can be directly deposited on the CNTs using a focused ion beam (FIB) (Ebbesen et al., 1996). These methods have been used to gain insight in the fundamental properties of CNTs (Ebbesen et al., 1996), but also to integrate isolated nanotubes as active elements in microsystems such as pressure sensors (Stampfer et al., 2006a). Nevertheless, these methods rely on a random dispersion of CNTs and are therefore limited to serial processing, which is not conducive to large-scale manufacturing.

- **Direct mechanical placement of CNTs:** Using nanomanipulators or AFM probes, it is possible to pick up CNTs and deposit them at a desired location to study their properties (Cumings & Zettl, 2000) or to integrate them directly in N/MEMS (Williams et al., 2002). Similar to the previous dispersion-deposition method, this approach is time consuming and difficult to integrate with batch fabrication processes; however, it is advantageous because individual CNTs can be placed precisely. The strength of interactions (e.g., electrostatic, van der Waals) is important for manipulating individual CNTs. This problem was addressed by Kim and colleagues, who developed a technique whereby individual CNTs are integrated in a micropellet, which facilitates the handling of the CNTs but also enables the use of parallel self-assembly techniques to increase the throughput (Kim, 2006).

- **Controlled CNT deposition from solutions:** Dielectrophoretic deposition of CNTs from a solution is a commonly used method to integrate CNTs on large numbers of microfabricated electrodes in parallel. In this approach, CNTs are first dispersed in a solvent (usually with stabilizing surfactant), and are subsequently directed to a predefined location on the chip using an electric field. While this method was first developed to deposit CNT films and simultaneously separate semiconducting CNTs (Krupke et al., 2004), it has been refined to deposit single, isolated CNTs (Chung et al., 2004; Vijayaraghavan et al., 2007). Experiments show this approach can achieve densities greater than 1 million/cm² of individually contacting SWNTs (Vijayaraghavan et al., 2007).

- **Direct growth of freestanding CNTs:** Using plasma-enhanced CVD and small catalyst island determined by e-beam lithography, freestanding vertically aligned carbon nanofibers can be fabricated. Freestanding CNFs have been used as field emission elements (Guillorn et al., 2001) and electrochemical probes (Guillorn et al., 2002). Alternatively, Hierold and colleagues demonstrated that CVD growth can also be employed to grow CNTs horizontally forming bridges between microelectrodes (Hierold et al., 2007), in the suspended configuration discussed in section 3.
4.3 Transformation and densification of CNT forests

When assemblies of CNTs are desired, a limitation to their bulk properties is their low as-grown density. Therefore, in order to improve the properties of bulk CNT forests, methods have been developed to increase the CNT density after growth. Two types of methods have been reported: A first approach consists of mechanically pushing CNTs together, while in a second approach CNTs are aggregated using surface tension to form dense vertical structures and other 3D geometries.

Mechanical rolling has the ability to simultaneously transform as-grown, low-density, vertically aligned (VA) CNT forests into higher-density, horizontally aligned (HA) CNT networks. The main challenges facing this process are to maintain CNT alignment, to minimize defects in the CNTs due to stresses developed during rolling, and to control the adhesion of the CNTs to the receiving substrate. One rolling method (Wang et al., 2008) uses a microporous membrane between a large diameter roller (~cm) and a CNT forest grown from a non patterned catalyst substrate. By aligning the membrane over the forest before rolling, the CNTs in the forest stick to the membrane after the rolling process due to van der Waals forces. The membrane with the HA-CNTs is then aligned on top of the receiving substrate (e.g., glass) such that the CNTs are facing the glass, then a solvent such as ethanol is poured from the top of the membrane. While the solvent is being evaporated, the CNT film transfers from the membrane to the receiving substrate and is further densified due to capillary action. In a second approach, researchers at Rice University (Pint et al., 2008) used photolithography to pattern the catalyst into 5-µm-wide gratings separated by tens of microns. The idea here is to grow the VA-CNTs then to mechanically roll them such that they slightly overlap to form continuous networks over the substrate area. The group also uses an intermediate foil (metal or polymer) between the roller and the CNTs to overcome adhesion problems to the roller. They indicate “shearing” the film along the CNTs before rolling in the same direction.

Finally, guided by the Hertzian contact stress theory, researchers at the University of Michigan (Tawfick et al., 2009) designed a force controlled rolling machine to transform CNTs, as shown in Fig. 7. The roller size and material is selected to ensure that the CNTs remain on the growth substrate without the need of intermediate foils or membranes. For successful transformation that preserves the CNT alignment without introducing destructive shear forces, the roller diameter must be smaller than the VA-CNT height and the linewidth of the catalyst must be significantly smaller than the roller diameter. These conditions avoid the formation of defects in the HA-CNT networks due to shear stresses caused by the rolling action. These results are confirmed by comparing Raman spectra of the CNT networks before and after rolling. The HA-CNT bundles are made of continuous CNTs having length up to one millimeter, and the thickness of the sheets can be tuned from hundreds of nanometers to several microns. The HA-CNT bundles can be transferred to polymer substrates (e.g. PDMS) using kinetically controlled (Meitl et al., 2006) peeling.
While the rolling process is performed after growth, it is also possible to influence the shape and density of CNT forests during growth. For instance, it has been demonstrated that CNT forests can be grown to conform to the shape of microfabricated templates (Hart & Slocum, 2006). This process is analogous to micromolding but employs the force generated by the growth process of the nanotubes to fill the templates.

It is also possible to aggregate CNTs using capillary forces. In this approach CNT forests are typically submerged in a solvent such as acetone or IPA, which aggregates the CNTs as it evaporates because the surface tension of the moving meniscus draws the CNTs together. This approach is particularly simple and versatile; it has been used to segregate CNT forests into cellular foams (Chakrapani et al., 2004; Correa-Duarte et al., 2004; Liu et al., 2004), to achieve isotropic contraction of CNT micropillars (Futaba et al., 2006), and to achieve
unidirectional toppling (Hayamizu et al., 2008) of CNT “blades” to create lateral films. However, a limitation of the immersion process is that the liquid meniscus can connect adjacent CNT structures, and connect CNT structures to the substrate, and this can damage small CNT forests which are typically fragile to the low density of the as-grown forests. To overcome this limitation, recent work shows that by condensing acetone on the structure instead of immersing it, it is possible to densify delicate CNT microstructures, and by carefully designing the initial shape of the forest, it is possible to fabricate complex 3D microstructures including sloped micro-wells, bent cantilevers, pyramidal microtrusses, and helical micropillars (De Volder et al., 2010). Examples of these structures are shown in Fig. 8. The same group also showed that the condensation densification method increases the Young’s modulus of CNT forests from 54 MPa to 5 GPa for densified forests. The latter exceeds the stiffness of commonly used MEMS polymers such as SU-8, and benefits from the outstanding electrical and thermal properties of CNTs.

Figure 8. Diverse 3D microarchitectures made by capillary forming of carbon nanotubes (De Volder et al., 2010) : (a) schematic of capillary forming process showing micro and nano-scale detail; (b) concentric wells and bending structures before and after capillary forming; (c) blooming flower of bending structures; (d) micro-helix made by combining contraction and bending operations.
4.5 Composite CNT microstructures
Extensive research has been performed on the dispersion of CNTs in polymers to increase their stiffness and fracture resistance or to obtain electrically conductive polymers. At larger scales, most work on CNT-based composites has focused on dispersion of SWNTs or MWNTs in a polymer matrix; however, bulk CNTs embedded in a polymeric matrix tend to form aggregates that are not only poorly adhered to the matrix but also concentrate stresses, compromising the effect of the CNTs as reinforcement (Thostenson et al., 2001; Garcia et al., 2007). Instead, Garcia et al. proposed to infiltrate vertically aligned CNT forests with polymers (Garcia et al., 2007). Due to the alignment of the CNTs, this method resulted in an increase in Young’s modulus of 200% after polymer infiltration. Combining this approach with the capillary densification process described above, Young’s moduli of 18 and 25 GPa have been achieved using SU-8 and PMMA as matrix polymer respectively (De Volder et al., 2010).

Vertically aligned CNT-forests have also been infiltrated with ceramics; for example, a CNT framework is filled with polysilicon and silicon nitride using LPCVD (Hutchison et al., 2009). The latter material was employed to fabricate high-aspect ratio microdevices including electrostatic and thermal actuators. This process could complement other high-aspect ratio MEMS processes such as DRIE and SU-8 processing.
5. Examples of CNT integration in N/MEMS

5.1 Electrical interconnects

Due to their high electrical conductivity and current-carrying capacity, metallic CNTs have been investigated as new materials for vertical interconnect vias. As microelectronics progresses to finer resolution, smaller-diameter interconnects are required and therefore these interconnects must handle a higher current density. Fujitsu projects that CNTs will be necessary for 32 nm linewidth processing and beyond, where the required current density will exceed $10^6 \text{ A/cm}^2$, and therefore crossover between CNT and Cu performance is expected between years 2010 and 2015.

Calculations predict that the resistance of a 70 nm diameter vertical via filled with close packed MWCNT of 4 nm diameter having 6 walls, can be as low as that of a Cu via. Fujitsu (Nihei et al., 2004; Horibe et al., 2005; Nihei et al., 2005), Infineon (Kreupl et al., 2002) and IMEC (Chiodarelli et al., 2010) reported progress in process technology to achieve this high performance, including direct growth of the CNTs within vias at CMOS-compatible temperatures followed by deposition of a top electrical contact. Fig. 9 shows this architecture, and Table 2 shows the most recently reported results from these groups.

![Integration and performance of vertical CNTs as microelectronic interconnects, by Fujitsu.](image)

Despite this encouraging progress, several challenges have to be met before CNTs can actually replace Cu interconnect vias. According to the 2009 International Technology Roadmap of Semiconductors (ITRS, 2009) the main challenges to overcome for vertical vias are:

1. Improved control over CNT diameter, number of walls and quality
2. Achieving high CNT areal density, e.g., at least $5 \times 10^{12} \text{ CNTs/cm}^2$ for MWNTs
3. Achieving ohmic contact to the ends of the CNTs

In order to realize high density growth at low temperatures researchers are decomposing the feedstock gas required for CNT growth using a multi-mode (RF plasma, DC plasma, hot-filament, and thermal) CVD chamber to scale up the process to obtain uniform growth on full 300 mm wafers. The catalyst nanoparticles are prepared either by dewetting a thin
catalyst layer (Co or Ni) through thermal annealing or by direct injection of catalyst nanoparticles from gas phase. Both of these variations aim at achieving the highest density of active nanoparticles selectively at the bottom of the via holes. More recently, Fujitsu reports a plasma-enhanced formation of small-diameter, closely packed nanoparticles from a deposited layer of Co. The key to their method is to control the nanoparticle size and density and to stop the aggregation of particles before the growth starts. This is achieved using a low temperature (<260 °C) and low-power plasma (<0.5 W/cm²) for annealing. The CNT density reaches 10^{12} CNTs/cm² representing a bulk volumetric density of 30-40%.

Table 2. Major milestones in development of vertical MWNT vias.

<table>
<thead>
<tr>
<th>Via dia.</th>
<th>CNT dia.</th>
<th>Stackup</th>
<th>Catalyst</th>
<th>Recipe</th>
<th>Density [CNTs/cm²]</th>
<th>Resistance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 µm</td>
<td>10 nm</td>
<td>Cu/Ta/Ti/Co/CNT/Ti/Cu</td>
<td>2.5 nm Co layer</td>
<td>thermal CVD 450°C</td>
<td>10^{10}</td>
<td>5 Ω</td>
<td>a</td>
</tr>
<tr>
<td>140-300 nm</td>
<td>15 nm</td>
<td>Cu/Al/Ni/CNT/AuPd</td>
<td>3 nm Ni layer</td>
<td>thermal CVD 520°C</td>
<td>5 x 10^{10}</td>
<td>20 Ω</td>
<td>b</td>
</tr>
<tr>
<td>2 µm</td>
<td>10 nm</td>
<td>Cu/Ta/TiN/Co/CNT/Ti/Co</td>
<td>4 nm Co nanoparticles</td>
<td>thermal CVD 510°C</td>
<td>9x10^{11} and 10^{11}</td>
<td>0.59 Ω</td>
<td>c</td>
</tr>
<tr>
<td>150-300 nm</td>
<td>8-12 nm</td>
<td>TiN/SiC/PSG/SiC</td>
<td>1.3 nm Ni Layer</td>
<td>CVD 400-470°C</td>
<td>2x10^{11} - 7x10^{10}</td>
<td>7.9 kΩ</td>
<td>d</td>
</tr>
<tr>
<td>120 nm</td>
<td>7 nm</td>
<td>Cu/TaN/Tin/Co/CNT</td>
<td>1.7 nm Co film</td>
<td>thermal CVD 450°C</td>
<td>10^{12}</td>
<td>not yet reported</td>
<td>e</td>
</tr>
</tbody>
</table>

a (Nihei et al., 2005)  
b (Coiffic et al., 2008)  
c (Sato et al., 2006)  
d (Chiodarelli et al., 2010)  
e (Yamazaki et al., 2010)
5.2 Emission sources: displays and X-ray emitters

Samsung Display Innovation, a division of Samsung Corporation spent several years developing a field emission display (FED) using carbon nanotubes (CNTs) as the field emission source. While this project has been discontinued prior to market introduction due to the emergence of LCD display technology, the design and manufacturing of the prototype CNT FED display serve as an excellent example of CNT integration in a consumer electronics application.

The Samsung CNT FED, shown in Fig. 10, was microfabricated on display glass and features a triode structure. In the triode structure, a bias voltage is applied between the bottom (cathode, ITO) and middle (gate) electrodes, and the emission is focused by the top electrode (Choi et al., 2006) (Fig. 3). The CNT emitters are applied to the device by screen-printing of a custom-made CNT paste, or by direct growth of CNTs by chemical vapor deposition (CVD). In the former case, commercially available CNTs are mixed with many ingredients, and the paste is wiped through a screen mask, which is placed over the device (Choi et al., 2004). In the latter case, a catalyst layer is deposited (e.g., sputtered invar) on the device and the CNTs are subsequently grown by thermal CVD of CO/H\textsubscript{2}. For screen printing of the paste, the maximum (and therefore limiting) process temperature is that of firing the paste after printing (<450 °C); for CNT growth the CVD temperature is limiting (lowest 420 °C so far; must be <500 °C to prevent melting of the glass). While isolated, vertically aligned CNTs as grown by the CVD process are desired for field emission, the CNTs in the paste are generally tangled and parallel to the substrate. Therefore, CNTs as-deposited by the paste method are aligned vertically by applying and peeling a tape from the substrate.

Figure 10. Samsung CNT field emission display a) schematics of display structure and triode pixel architecture. b) SEM image of individual pixel with aligned CNTs grown directly on substrate, and image of prototype 15” diagonal display.
The use of CNTs as X-ray emission sources has been pioneered by the group of Prof. Otto Zhou at the University of North Carolina, and is being commercialized by Xintex, Inc. In a CNT-based X-ray source CNTs are placed in a triode configuration as a field electron emitter, and the emitted electrons are incident upon a target (typically Mo), which in turn emits X-rays and is aimed toward the sample (Cheng et al., 2004). Overall, imaging systems using CNT X-ray emitters offer promise over current technology due to their small size, fast response time, and capability for multiplexing and array imaging. These seek to enable rapid, high-resolution imaging without the need for moving the source and/or detector as is typical in many current X-ray and CT imaging systems. Like with field emission displays, CNT X-ray emitters can be arrayed as “pixels”, and imaging is facilitated by the rapid response time of the emitters along with frequency division multiplexing using a single flat detector (Zhang et al., 2006). CNTs can be integrated in X-ray emitters by direct growth on the emitter substrate, or by post-growth deposition, and therefore face similar manufacturing challenges as field emission displays, although displays require further integration with circuit architectures and immediately need finer pixel resolution. In a prototype device, purified SWNTs were deposited from solution to give a tangled CNT morphology on a metal substrate, which was then incorporated in a sealed emitter tube (Zhang et al., 2005).

5.3 Chemical sensors

The high electrical conductivity and surface area of CNTs is motivating their application as chemical sensors. Examples include detection of trace contaminant and hazardous vapors for industrial process control and security applications, and for breath analysis in medical diagnostics (Snow et al., 2006). This is particularly true for SWNTs, which a high specific surface area and therefore are most sensitive to the presence of nearby molecular species and molecular adsorbates. Typically, a CNT-based chemical sensor consists of a tangled network of CNTs, which are electrically connected to a substrate (Fig. 11): in a resistive sensor, the CNTs are connected between electrode pairs such as interdigitated fingers; and in a capacitive sensor the capacitance between the network and the substrate (isolated by a dielectric layer) is also monitored. Chemical adsorption on a CNT surface is driven by the partial pressure of the analyte relative to its vapor pressure (rather than relative to the ambient pressure); therefore, CNT sensors can detect low concentrations of low-vapor-pressure analytes such as explosives, where many conventional sensors are unable to do so.

Kong and colleagues demonstrate that adsorption of a molecule on the surface of a SWNT causes a transfer of charge (i.e., donation or withdrawal of an electron) to the SWNT and therefore changes its electrical conductivity (Kong et al., 2000). Many adsorbates bind strongly to CNTs, and the sensor was heated or exposed to ultraviolet light to remove the adsorbate from the CNT surfaces and therefore “zero” the signal. Further, the sensitivity of a CNT to charge-transfer interactions (i.e., how many electrons are transferred/withdrawn per adsorbed molecule) depends on the electronic structure (i.e., chirality) of the CNT and adsorbed molecule. A general strategy to increase sensitivity (i.e., minimum detectable concentration) and/or specificity (i.e., response to a particular desired species) is to coat the CNTs with a polymer that selectively adsorbs a particular molecule or class of molecules. For example, coating a SWNT network sensor with polyethyleneimine (PEI) allows detection of 100 ppt of NO₂ in a response time of 1000 s (Pengfei et al., 2003). As an aside, while the sensitivity of electrical conductivity to surface adsorbates can be helpful for CNTs as
chemical sensors, it is important to consider these “environmental” effects in the context of stable operation of CNTs as other device elements such as transistors (Collins et al., 2000).

Figure 11. a) Typical architecture of a chemical sensor using a CNT network, where tangled CNTs are in contact with interdigitated electrodes, and the conductance and capacitance of the network is measured using external circuitry (Snow et al., 2006) b) A SWNT sensor’s conductance response to doses of NO2. The sensor was reset by exposure to ultraviolet light between doses and exhibits sensitivity of 100-parts-per-trillion.

The resistivity of a SWNT can also change due to collisions with gas molecules. This has been demonstrated by measuring a resistance increase across CNT network devices upon exposure to inert gases (Romero et al., 2005). This change is proportional to the molecular mass of the gas (as $M^{1/3}$), so a heavier molecule makes a larger “dent” in the sidewall of the CNTs. The authors hypothesize that the collisions introduce a new channel that scatters conduction electrons travelling through the CNTs. Since this phenomenon depends on the ambient composition and temperature it may require consideration for high-precision gas sensing using CNTs.

Adsorbed gases can also be sensed by measuring the capacitance of a CNT network; compared to resistive sensing this method is faster and responsive to a wider variety of vapors. When an electric field is applied between a CNT network and the underlying “gate” electrode, molecules adsorbed on the CNT surface are polarized, and this increases the capacitance between the network and the gate (Snow et al., 2005). With a minimum (reversible) detectable capacitance change $\Delta C/C = 10^{-4}$, part-per-billion detection limits for nerve agent and explosive vapors are expected (Snow et al., 2006). Simultaneous resistive and capacitive sensing can further identify vapors based on their relative responses (Snow & Perkins, 2005), and detection algorithms such as those using artificial neural networks are sought to identify analytes from the outputs of sensor arrays (Shi et al., 2006). For CNT sensors, resistive sensing is preferred for analytes that give a large charge transfer, and capacitive sensing is better for analytes that transfer less charge as it offers increased sensitivity, larger dynamic range, and faster response (Snow et al., 2006).

For commercial viability, CNT sensor systems must reliably detect and identify target vapors in ambient atmospheres containing many other species and under varying temperature and humidity. Therefore, further development of sensor arrays along with chemically specific coatings, pre-concentration techniques, and signal analysis algorithms is necessary. More complex techniques such as mass spectrometry and ion mobility
spectrometry will likely maintain superiority for chemical analysis and non-specific agent detection, and CNTs offer opportunities in miniaturization of these systems as well.

5.4 Electromechanical devices and transducers

Nanoscale electromechanical transducers have attracted significant attention for advancing current device technology toward high-sensitive, low-power sensors. Further, as architectures continue to scale down, devices are approaching the quantum limit for detecting non-classical states of mechanical motion (Hierold et al., 2007), which holds significance for fundamental scientific research. In order to realize these scalability and performance, we require new materials with exceptional properties.

While CNTs have many exciting properties, one of the most promising characteristics for small devices is the coupling between their electrical transport and mechanical deformation. This piezoresistive characteristic in conjunction with inherently high elasticity makes CNTs strong candidates for nanoscale electromechanical transducers, since they can endure significant deformations yet return to their original states.

Based on these principles, several prototype devices with integrated CNTs for transduction have been developed (Hierold et al., 2007; Jungen et al., 2007a), including electromechanical sensors for measuring mass (Stampfer et al., 2007), force (Stampfer et al., 2006b), and pressure (Wood & Wagner, 2000; Sickert et al., 2006; Stampfer et al., 2006a). Examples of these devices are shown in Fig. 12. Specifically, a single suspended SWNT was implemented as the transducer element in a microfabricated pressure sensor, where deflection of a suspended Al₂O₃ membrane strains the SWNT and thereby changes its I-V characteristics (Stampfer et al., 2006a). Gauge factors up to 1000 have been exhibited (Cao et al., 2003). Other investigations were aimed at understanding the transduction mechanism and especially how the electronic band structure of SWNTs is altered under mechanical strain, either axially or due to curvature (Minot et al., 2003; Grow et al., 2005). Earlier, telescoping “sword-in-sheath” extension of a MWNT provided a demonstration for a nanoscale linear bearing, having no measurable wear between the sliding wall surfaces (Cumings & Zettl, 2000). Extending this idea, a telescoping MWNT is built as a tunable electromechanical resonator, having ∼200 MHz oscillation frequency (Jensen et al., 2006).
Figure 12. a) Schematic representation of a NEMS with an integrated SWNT by direct growth and a comb drive for sensing/actuation. The SEM image shows a freestanding SWNT bridging two poly-Si tips. b) Schematic concept illustration of a SWNT-based nanoscale sensor system, which may be used for measuring the electrical response to mechanical deformations applied at the center cantilever via an AFM tip. The SEM image shows a SWNT bridging two electrodes with the center cantilever exerting a force downward on the SWNT. c) Schematic of a CNT-based pressure sensor consisting of an ultrathin Al₂O₃ membrane with a SWNT adhering to the membrane with electrodes. SEM images of the device show electrodes extending onto the membrane (black circle) and electrically contacting a SWNT (left image), which is shown at higher magnification in the right image.
Although single CNT devices have not become commercially viable, the only known mass-produced electromechanical device using CNTs is the nanotube memory “NRAM” developed by Nantero, Inc. The NRAM concept was conceived and demonstrated as a “crossbar” architecture where each bit is a cross-junction between isolated SWNTs. This bistable configuration can be actuated electrostatically and interrogated by reading the electrical resistance of the junction (Rueckes et al., 2000). Because it is so far impossible to fabricate a large crossbar array by either direct growth or post-growth manipulation of CNTs, commercialization of this idea realized the device using a suspended-ribbon architecture, where a membrane (1-2 nm thick) of CNTs is electrostatically deflected to contact a bottom electrode, where it reversibly adheres to the electrode due to van der Waals interactions. In 2006, Nantero reported that NRAM devices have been switched over 50 million cycles, at operating voltages below 5 V, with switching times below 3 ns. While flash memory has dominated the commercial market, the robustness of CNTs makes the NRAM architecture attractive for harsh environments.

A further important commercial aspect of Nantero’s effort is the integration of CNTs into a CMOS process, where SWNTs are purified and dispersed in a solvent, and then the solvent is coated onto wafer substrates and can be subsequently patterned and etched using lithographic techniques. Within tangled CNT film geometries, such a “CNT photoresist” will be vital to CMOS-compatible fabrication of other devices including digital logic, reconfigurable antennas, and sensors without necessitating CNT growth; however, as emphasized earlier direct deposition is unlikely to achieve highly ordered CNT assemblies.

5.6 Thermal interface materials

As the size of microelectronic circuits and devices continue to scale down and their power increases, efficient thermal management becomes more crucial. Since mating two rigid surfaces together is inherently limited by finite surface roughness (Fig. 14a), an effective thermal interface material (TIM) is desirable for minimizing thermal contact resistance between the device and heat sink in order to maximize thermal dissipation. A good TIM
therefore fills the gaps between contacting surfaces and provides high thermal conductivity (Gwinn & Webb, 2003). These requirements are difficult to meet because materials having high thermal conductivity are typically hard solids, and it is difficult to maintain good contact between hard solids especially under thermal cycling which occurs during microprocessor operation.

![Figure 14](image)

Figure 14. a) Schematic drawing of the mating of two rough, rigid interfaces (i.e., a device and a heat sink) with a thermal interface material between them. Note the gaps between the TIM and the rough surfaces (Gwinn & Webb, 2003). b) Conceptual drawing of similar surfaces bridged by a CNT forest as a TIM, where the compliance of the forest enables greater thermal contact between the TIM and the rough surfaces. c) Thermal resistance model for these proposed systems, which is also described by Eq. 1.

While the ideal TIM has yet to be discovered, CNTs are among the promising candidates (Huang et al., 2005; Tong et al., 2007) because they can potentially provide outstanding heat transport while CNT assemblies can be designed to maintain conformal contact against rough surfaces (Fig. 14b).

If the governing equation for the thermal resistance of an interface is expressed as

\[
R = R_{contact1} + R_{TIM} + R_{contact2}
\]

and \(R_{TIM} = R_{CNTs}\), then \(R\) may vary significantly (Fig. 14c). CNT forests in particular are interesting for this application since they have inherently high alignment (Fig. 15a), which can provide many direct thermal conductance pathways, but challenges arise due to varied morphologies that evolving during forest growth. For instance, in Fig. 15b, we show the disordered morphology at the base of a CNT forest, which correlates to the end of the growth process (Meshot & Hart, 2008; Bedewy et al., 2009; Meshot et al., 2010). In principle, the two contact resistances are dictated primarily by the number density of CNTs, where a larger density provides more conduction pathways (Fan et al., 2009). However, given that Prasher, et al. has proven that contacts between neighboring CNTs within an ensemble hinders the net thermal conductivity (acting as parasitic resistance) there is presumably an optimal number density past which, the number of CNT-CNT contacts can limit the net conductivity.
Figure 15. SEM images of a typical CNT forest taken at the a) middle and b) base of the sidewall. Note the distinct morphological change from top to bottom of the forest (beginning to end of growth). Inset to (a) shows photograph of a millimeter-tall forest adhered to its Si substrate (Meshot et al., 2010).

Thus, for this application, vertically aligned forests of CNTs are highly advantageous since their orientations are predominantly parallel to the conduction pathway, with fewer CNT-CNT interactions than in a disordered CNT film. Still, considering that as-grown forests typically range from 1-5% density, even perfect scaling of individual CNT properties results in bulk conductivity estimates less than Cu. Experiments have shown that densifying a forest, either mechanically or by capillary forces, increases the thermal conductivity from as low as 8 W/m-K to as high as 2369 W/m-K (Akoshima et al., 2009). Also, progress toward infusing a filler material (e.g., polymer) suggests that reducing the volume of air in the pores of the forest may enhance the thermal conductivity (Ivanov et al., 2006; Duong et al., 2009), but so far enhances are practically marginal. The limitations may arise due to CNT-CNT contacts as well as interfaces between CNTs and the filler material, both of which will induce additional phonon scattering during thermal energy transport, which leads to decreased conductance.

7. Conclusions and Outlook

Functional integration of CNTs in miniaturized systems requires control of the synthesis and organization of CNTs at hierarchical length scales spanning from the dimensions of individual CNTs to the dimensions of wafer substrates. Combined with constraints of microfabrication, including CMOS temperature limits and resistance to liquids and plasmas, it remains challenging to grow, place, and contact CNTs in a manner that meets manufacturing requirements. Further, while the exceptional properties of CNTs have been verified in all categories, prototype CNT devices provide many examples where sacrifices in properties due to non-ideality of CNT quality, density, and alignment, are apparent. Nevertheless, profitable demonstrations of CNTs as interconnects, non-volatile memory, inertial sensors, and thermal interfaces have been made and are on the path to commercialization. Further advances in low-temperature CNT growth, chirality separation
and control, and directed self-assembly of 3D CNT structures will pave the way for new applications in the coming years, along with broad use of CNTs as a new microfabrication material. The future is certainly bright for continued innovations in the science and applications of CNTs.

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9. References


Duong H., Yamamoto N., Papavassiliou D., Maruyama S. & Wardle B., Inter-Carbon Nanotube Contact in Thermal Transport of Controlled-Morphology Polymer Nanocomposites. *NANOTECHNOLOGY* 2009; -.


MEMS and Nanotechnologies: From Science-to-Electronic Systems


