High-Performance Semiconducting Nanotube Inks: Progress and Prospects

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ABSTRACT While the potential for high mobility printed semiconducting nanotube inks has been clear for over a decade, a myriad of scientific and technological issues has prevented commercialization and practical use. One of the most challenging scientific problems has been to understand the relationship between the pristine, individual nanotube mobility (known to be in the range of 10 000 cm²/V·s) and the as-deposited random network mobility (recently demonstrated in the range of 100 cm²/V·s). An additional significant hurdle has been to understand, manage, and ultimately eliminate the effects of metallic nanotubes on the network performance, specifically the on/off ratio. Additional scientific progress is important in understanding the dependence of nanotube length, diameter, and density on device performance. Finally, the development of ink formulations that are of practical use in manufacturing is of paramount importance, especially with regard to drying time and uniformity, and ultimately, the issue of scalability and cost must be addressed. Many of these issues have recently been investigated from a phenomenological point of view, and a comprehensive understanding is beginning to emerge. In this paper, we present an overview of solution-based printed carbon nanotube devices and discuss long-term technology prospects. While significant technical challenges still remain, it is clear that the prospects for the use of nanotube ink in a myriad of systems is feasible given their unmatched mobility and compatibility with heterogeneous integration into a variety of applications in printed and flexible electronics.

KEYWORDS: semiconducting carbon nanotube · solution-based deposition · random network · thin film transistor · mobility · on/off ratio · nanotube network density · radio frequency · circuit demonstration

What is the fundamental performance limit of carbon-nanotube-based semiconducting inks? The answer to this question lies ultimately with the atomic structure of an individual single-walled carbon nanotube (SWNT), composed of a sheet of graphene (sp² carbon honeycomb lattice) rolled into a seamless cylindrical shape. On the basis of the cut and degree of twist of the graphene sheet (the chirality, specified by two indices (n,m)), SWNTs exhibit either metallic or semiconducting behavior. Owing to their unique materials properties related to the one-dimensional nature of electron transport, carbon nanotubes have been proposed for different electronic applications including RF devices, digital logic circuits, interconnects, and conductive sheets. However, the key challenge which occurs over and over in all of carbon nanotube science and technology is the ability to economically control the position and composition of macroscopic numbers of nanotubes in a way that preserves the outstanding electrical properties of pristine, individual SWNTs.

Several approaches have been tried to demonstrate different fabrication techniques for depositing nanotubes at preferred locations on substrates in order to obtain high-performance nanotube-based circuits and devices. On the basis of the process involved, these different approaches can be divided into two major categories: "grow-in-place" and "solution-based (nanotube ink)". The grow-in-place technique allows simultaneous synthesis and deposition of nanotubes with moderate to excellent control of alignment (depending on the substrate). Significant and substantial challenges remain in controlling the ratio of semiconducting to metallic carbon nanotubes (typically 2:1, not sufficient for high-performance electronics) and in controlling the nanotube diameter and chirality. While a combination of substrate-controlled alignment and deposition control leads to atomic alignment with good semiconductor to metal ratios of ~10:1 in certain substrates (recently reviewed for ultrahigh performance devices in ref 2), the generalization of this technique to other substrates and its wafer scalability has not yet been demonstrated.

In contrast, extensive progress has been made in postgrowth purification of SWNTs, leading to the prospect of a manufacturable and purification technology capable of delivering monodispersed SWNTs in solution of all the same chirality, diameter, length, and also (hence) type (semiconducting vs metallic). While such a goal is not yet demonstrated (progress was reviewed in refs 8 and 9), commercial and academic sources already are able to provide 99% semiconducting nanotube material. It is the
availability of this all-semiconducting nanotube material that has given rise to the prospect of a high-performance semiconducting ink, with mobilities that rival or even exceed the best available commercial semiconducting inks\textsuperscript{11} by orders of magnitude. It is the purpose of this article to review the challenges and opportunities in the use of these purified semiconducting materials as semiconducting inks and to provide a comprehensive survey of what is known and what still needs to be understood for this technology to be transitioned from academic curiosity to industrially relevant, high-performance systems. In order to achieve this goal, a thorough understanding of the performance projections of nanotube inks is critical, specifically regarding manufacturing yield, reproducibility, cost management, and optimized performance (such as mobility, on/off ratio, transconductance, high frequency, etc.).

The fundamental starting point for projecting the mobility of material deposited from such inks is the mobility of an individual, pristine SWNT. The pristine, individual nanotube mobility (even for individual nanotubes deposited from solution) is known to be as high as 10,000 cm\textsuperscript{2}/V s (depending on the diameter),\textsuperscript{12,13} and the as-deposited random network mobility has recently been demonstrated in the 100 cm\textsuperscript{2}/V s range.\textsuperscript{14} The reason for this apparent discrepancy is that the nanotube inks result in a random network of SWNTs. A recent comprehensive study was initiated\textsuperscript{14} using commercially available materials on the relationship between mobility, on/off ratio, and SWNT density, but a more complete understanding must await a more ambitious study of the interaction between all of the important materials parameters (such as nanotube chirality, length), the separation and deposition processes and chemistries (surfactant,\textsuperscript{15} substrate\textsuperscript{16}), and the final electrical and hence system properties (mobility, on/off ratio, cutoff frequency). The interconnections between all of these variables are indicated schematically in Figure 1.

It is for this purpose that, in this paper, we present a comprehensive overview of the current scientific and technological understanding of carbon nanotube semiconducting inks. Theoretical and computation models relating the alignment and composition of nanotube networks are analyzed and benchmarked against experimental data in the literature. However, most progress to date has come from phenomenological studies, thus motivating a comprehensive survey of the existing technical field from an experimental point of view. On the basis of this comprehensive overview, obstacles and proposed solutions for practical applications are discussed, leading finally to the potential future applications of carbon-nanotube-based electronics in the growing market of printed and flexible circuits and systems.

**VOCABULARY:**

- **Diffusive Transport** – Movement and transportation of carriers in the presence of scattering sources
- **Mobility** – A definition to characterize the movement of charge carriers (electron or hole) in any material when an electric field is applied
- **On/Off Ratio** – The ratio of the on-state current to the off-state current of a transistor. In electrical circuits, especially in digital systems, it is important to have as low OFF current as possible since the OFF current corresponds to the static power consumption of the circuit.
- **Cut-Off Frequency (f\textsubscript{c})** – The frequency at which the current gain becomes 1 (i.e., 0 dB)
- **Maximum Frequency of Oscillation (f\textsubscript{max})** – The frequency at which the available power gain drops to unity (i.e., 0 dB).

**Nanotube Synthesis and Purification: State of the Art and Prospects.** The starting material for nanotube-based inks can be synthesized with a variety of techniques. The most popular are chemical vapor deposition (CVD) and laser ablation. Generally speaking, these techniques involve a gaseous hydrocarbon feedstock at elevated temperatures, interacting with a catalytic nanoparticle. Typically, the average SWNT diameter can be controlled with some success,\textsuperscript{17–20} but the chirality is more difficult to control during synthesis. In the case of completely random chirality (which is typical for most synthesis methods), the resulting distribution of SWNTs contains a heterogeneous mixture of semiconducting and metallic SWNTs, with a mixture of 2/3 semiconducting and 1/3 metallic. This presents a severe problem for nanotube electronics, as the metallic nanotubes can short the semiconducting ones in the case of a random mat of the material. Some progress has been achieved in controlling chirality during the growth,\textsuperscript{21–23} although challenges remain. For example, some work has shown a predominance of (6,5) nanotubes (over 50% in some cases).\textsuperscript{22} In general, for small diameter SWNTs, if the diameter control is reasonable, then the number of possible chiralities is only a handful. However, for larger diameter nanotubes, the available (n,m) indices for a specific diameter are much larger (in the dozens), increasing the challenge of controlling the fraction of nanotubes of a specific chirality in the as-grown material. While it is clear that a large nanotube diameter is important for the development of low-resistance metal–nanotube contacts,\textsuperscript{24,25} its role in the properties of semiconducting ink is unclear. Therefore, there seem to be significant challenges in synthesizing SWNTs of the same chirality in the near future, and it is unclear what routes will be able to achieve this. Although speculative, one long-term route would use synthetic biology to develop an alternative, enzymatic synthesis process (a so-called “nanotube synthase”\textsuperscript{26}), mimicking the atomic precision of biology. The prospect of this is quite long-term and difficult to achieve. One does not even know where to start.
Because of the daunting synthesis challenges, it seems that the most likely development of near-term practical applications is the use of postgrowth purification technologies. By and large, these have had extraordinary progress in the last 5 years, with a variety of techniques showing varying degrees of success in taking raw, as-grown SWNT material and converting it into highly refined, purified solutions in lab experiments of SWNTs of a specific diameter and chirality.\(^8\)\(^9\) Already, commercial sources of purified semiconducting nanotube material are available for laboratory-based experiments. Therefore, the development of nanotube semiconducting inks is a realistic and feasible prospect for a variety of technological applications in electronics.

Purification technologies fall into a couple of categories: flow-based sorting (chromatography and electrophoresis/gel-based methods) and density-gradient ultracentrifugation\(^27\) (DGU). The centrifugation sorting has been shown to allow separation of metallic from semiconducting nanotubes, based on differences in their buoyancy in response to different surfactants and functionalization chemistries in differing solvents.\(^8\)\(^9\) A variety of surfactants have been explored for this application, and the state of the art allows for reproducible 99% semiconducting solutions to be prepared. This seems the most logical starting point for nanotube-based semiconducting inks and is the most studied and understood to date. The issue of cost and yield for this technique still needs to be addressed, especially as it is a batch process. A complementary purification technique relies broadly speaking on flow-based sorting techniques. This can be in the form of chromatography or gel and/or field-based sorting. Chromatographic techniques have the potential advantages of continuous flow process, which may be lower cost, although this has not yet been determined.

These techniques have been shown to be capable of separating nanotubes not only by their type (semiconducting vs metallic) and diameter but also by their chirality. Specific \((n,m)\) indices can be extracted from a heterogeneous population. The process relies in many cases on preferential binding of specific chemical moieties to specific \((n,m)\) indices. While a variety of binding moieties can be imagined, designed \textit{de novo}, and tested, it is an even more exciting prospect to use known chemistry and analytical techniques of molecular biology to sort based on DNA.\(^28\) Recent work\(^29\)\(^30\) has shown that DNA can bind with specific affinity to specific SWNTs, in a way that depends on both base pair sequence and SWNT \((n,m)\) index. Length-based sorting using DNA is also possible, allowing study of nanotube length on electrical properties of networks.\(^31\) Recently,\(^32\) our group assayed the binding of amino acids to SWNTs, screening all of them, and finding SWNT-specific amino acids that bind with specific affinity to SWNTs, with tryptophan the strongest binder. (This was verified by a different technique in ref 33.) There, we proposed to find or design peptide motifs with specific affinity to SWNTs of specific \((n,m)\) index. This was actually carried out recently through a massively parallel bioinformatics screen of the entire protein data bank (PDB) followed by assays of a select subset of candidate motifs.\(^34\) Thus, given the rapid pace of progress, it seems feasible that sorting technology will soon advance to the next level, and that purified solutions of SWNTs of a specific \((n,m)\) index (rather than just a specific type) will be available at a

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**Figure 1.** Overview of the carbon-nanotube-based electronics process from the base material to device-level application: ink chemistry and purification (left),\(^1\)\(^8\)\(^27\) nanotube network deposition and formation (middle),\(^7\)\(^14\)\(^46\) and electrical properties of the devices including "mobility", "on/off ratio", and "cut-off frequency" (right).
commercial scale for prototype development. This will open a new window for studies and demonstrations of monodisperse SWNT solutions. Such a material would have tailorable properties for a variety of applications.

The challenge, then, is economical sorting. However, once that is solved, there is still a much bigger issue of deposition and electronic properties of SWNT networks postdeposition, which we turn to next.

Electronic Properties of Nanotube Networks: Theoretical Background. The wide variety of parameters affecting the performance of nanotube networks makes it difficult to explore the response of such devices based on computer-aided simulation tools. Among these parameters are the length and diameter of nanotubes, chirality and electrical characteristic of each tube (semiconducting or metallic purity percentage of the network), channel length and width, electrode contact resistances, tube—tube junctions, alignment degree (if applicable), and network density, which all should be considered to predict the functionality of printed devices made out of nanotube networks. For this reason, most progress to date has been based on phenomenological and experimental investigations of device performance. In the following sections, we describe the predicted impact of the most important parameters on the ultimate electronic properties of nanotube networks, starting with the material properties, and ending with the system level performance. In this paper, we are generally interested in devices longer than the average nanotube length, that is, longer than about 1 μm. In this case, the network is a random network of metallic and semiconducting nanotubes, which must be modeled as such. This leads to scaling laws that differ from classical semiconductor MOSFET-type devices, which we now expand upon.

Percolation Theory

Scaling with Length. The most comprehensive model that exists is based on percolation theory, developed by Alam and colleagues at Purdue.\textsuperscript{35–42} The theory models the nanotube network as a random array of semiconducting and metallic nanotubes, with a fixed tube—tube conductance of 0.1 e²/h. The metallic nanotubes are on all the time, and the semiconducting nanotubes can be gated on and off. This model explains a large quantity of data, although (as we argue below) some significant anomalies remain. Reasons for this can include many effects that are difficult to incorporate into a simple model, such as tube—tube resistance, unknown distribution of nanotube chiralities and lengths in the network, effects of surfactants and functionalization on electronic properties, or the possibility of gating defects in metal SWNTs.

We begin with a classical discussion of pure semiconducting nanotubes, postponing a discussion of metallic nanotubes to later. In a classical 2D conducting film, the ON current is inversely proportional to source—drain (or channel) length ($L_{SD}$). In a system close to percolation threshold, this is not the case. For densities near the percolation threshold, there are many nanotubes that are not involved in the current carrying process. These tubes form new percolating paths as $L_{SD}$ reduces, and therefore, the effective current increases faster with $L_{SD}$ than the classical scaling law. For very high densities, the classical scaling holds. This scaling law can be expressed quantitatively as

$$I_{ON} \sim \frac{1}{L_{CNT}} \left( \frac{L_{CNT}}{L_{SD}} \right)^m$$

Here $L_{CNT}$ is the average nanotube length, $L_{SD}$ is the channel length (source—drain spacing), and $m$ is a universal constant which only depends on the normalized coverage ($\mu L_{CNT}^2$, $\mu$ corresponding to the density of nanotubes per unit area). For high-density networks, obviously, the network behaves like a classical conductor and $m \approx 1$. On the other hand, for densities near the percolation threshold, $m$ approaches 2 and then diverges as the density approaches zero. For moderate network density, $m$ is typically between 1 and 2. Researchers have used fits to the power law to infer what region of percolation the device is operating in (near percolation, or very dense).

Definition and Measurement of Mobility. While classical percolation theory is applied typically in the linear response regimes (small source—drain voltages), important device operation occurs at large source—drain voltages. Alam\textsuperscript{36} has generalized the theory for all regimes and has predicted that the I–V curve should scale as

$$I_{DS} = \mu_0 W C_{ox} L_{CNT} \left( \frac{L_{CNT}}{L_{SD}} \right)^m (V_{GS} - V_{th})^2$$

where $C_{ox}$ is the capacitance per unit area, $V_{GS}$ the gate—source voltage, $V_{th}$ the threshold voltage, $W$ the width, and $\mu_0$ the “mobility”, to be discussed next. Note that Alam does not parametrize it this way and only discusses the scaling law, not the prefactor, which we propose here to interpret as follows: In the limit of very dense networks, well above the percolation threshold, the exponent $m$ is 1, and hence the theory reduces to the classical theory, given by

$$I_{DS} = \mu_0 W C_{ox} (V_{GS} - V_{th})^2$$

We now consider the measurement and definition of mobility. In classical transistors, eq 3 holds for all conditions, so the mobility can be “measured” by using experimental values for $dI_{DS}/dV_{GS}$ in the small signal (small source—drain voltage) limit as

$$\mu_{\text{measured}} = \frac{dI_{DS}}{dV_{GS}} \frac{1}{V_{DS}} \frac{1}{C_{ox} W}$$
or (in the large $s$–$d$ voltage limit) by a fit to eq 3 (i.e., assuming that $m = 1$ in eq 1). For classical semiconductor devices, both methods typically give the same result. However, in nanotube network devices, this is not always the case, so one must interpret the measurement of mobility with care. Almost all mobility calculations presented in the literature are based on the curve fitting to the linear region (low $V_{DS}$), but it is important to note that the actual operating region of the devices is in the saturation region.

In the high density limit ($m = 1$), eq 2 reduces to eq 3, so the measured mobility (given by $\mu_0$ from eq 2) can be interpreted as a classical, scale-independent mobility. However, nearer to the percolation threshold, the measured mobility from eq 4 is actually given by (using the parameters in eq 2):

$$\mu_{\text{measured}} = \mu_0 \left( \frac{L_{\text{CNT}}}{L_{\text{SD}}} \right)^{m - 1}$$  \hspace{1cm} (5)

Thus, percolation theory predicts a “measured mobility” (which is what is quoted in the literature) that would scale as $\sim 1/L_{\text{SD}}$ in the percolation limit. This is actually NOT what is universally observed (see Figure 4b), so the theory, while a good general framework, does not predict all of the scaling laws observed. In addition, eq 1 is obeyed in published scaling laws measured by Alam and collaborators,38,41 and others33–46 on mixtures of metallic and semiconducting nanotubes but not by all-semiconducting nanotube devices.47

**Capacitance.** The capacitance coupling $C_{\text{ox}}$ introduced in this equation is also much different than that of classical thin film materials. For nanotube-based transistors, this capacitance mainly depends on the density of the network (separation between nanotubes), distance between the gate and the channel, diameter of the nanotubes, and the intrinsic quantum capacitance of nanotubes. A semiquantitative model of the gate capacitance can be estimated for a network consisting of a parallel array of nanotubes with equal tube–tube distance.48 An analytical expression of the gate capacitance based is given by

$$C = \left( \frac{1}{\sigma_0 C_0} \right)^{1-m} \ln \left[ \frac{\sigma_0}{\sigma} \sinh \left( \frac{2\pi \tau_{\text{ox}}}{\lambda_0} \right) \right]^{-1} \frac{1}{\Lambda_0^{-1}} \left( \frac{2\pi \tau_{\text{ox}}}{\lambda_0} \right)$$  \hspace{1cm} (6)

where $t_{\text{ox}}$ is the oxide thickness, and $\Lambda_0$ is the tube–tube separation, $R$ is the tube radius, and $C_0$ is the quantum capacitance. As mentioned above, eq 6 is mainly used for aligned (parallel) network of nanotubes, and therefore, for random arrays, it is expected to be a qualitative guide but not to hold quantitatively. This capacitance modeling is significant in calculating the mobility of nanotube network films for different densities. Taking this capacitance into account, one can obtain more precise determination of the mobility.

**Alignment.** The network’s alignment is an important parameter in defining the performance of the nanotube-based transistors. In general, for short channel devices (compared to the nanotube average length), better alignment yields higher current. However, for channel lengths much longer than the nanotube average length, perfect alignment, in fact, precludes any current flow at all. Therefore, there exists a practical optimum level of alignment, which depends in a complex way on the device geometry. In fact, for long channel nanotube transistors, a random network is, in some cases, close to being optimal.39 Simulations show that the current is maximum at an alignment degree somewhere between perfectly aligned and perfectly random network of nanotubes. Indeed, for aligned networks, since the average tube length is much less than the channel length, the probability of nanotubes bridging from source to drain decreases drastically as the alignment degree increases. Thus, one only expects a modest performance improvement with increasing alignment.

**On/Off Ratio.** The on/off ratio is important in defining the power consumption of devices when used in digital circuits. In a mixture solution of nanotubes, the ON current corresponds to both types (metallic and semiconducting) of tubes while only metallic tubes are responsible for the OFF current. The model used by most researchers assumes that the ON current scales with length as eq 1 above, with $m$ the exponent corresponding to the total density of the nanotube network (both the metallic and semiconducting nanotubes). In the off state, eq 1 still applies but only for the metallic density, so that the exponent $m$ is different. (Recall that $m$ depends on the network density.) These two differing exponents (corresponding to the two different densities) are labeled as $m_{\text{on}}$ and $m_{\text{off}}$. Since the ON and OFF current scale differently with channel length, these percolation models predict that the on/off ratio ($R$) scales as

$$R \sim \left( \frac{1}{L_{\text{SD}}} \right)^{m_{\text{on}} - m_{\text{off}}}$$  \hspace{1cm} (7)

with $m_{\text{on}} < m_{\text{off}}$. Therefore, the on/off ratio exponentially ($m_{\text{on}} - m_{\text{off}}$) increases as a function of $L_{\text{SD}}$. This model seems to describe much data of random mixtures of semiconducting and metallic nanotubes quite well.38 In purified networks, since the density of metallic nanotubes is small, the on and off scaling exponents are almost identical, that is, $m_{\text{on}} \approx m_{\text{off}}$, and it is predicted that the on/off ratio should be nominally independent of channel length. While some length dependence is still observed, this reduced dependence of on/off ratio on gate length seems well-described.38

**Fundamental Limits.** In general, it is known that the mobility of an individual, pristine semiconducting...
nanotube (even for individual nanotubes deposited from solution) can be up to 10,000 cm²/V·s (depending on the diameter). It should be noted that this mobility is achieved with nanotubes long enough to bridge the entire distance from source to drain. However, mobilities for random networks of carbon nanotubes (the focus of this review) have hovered until recently around the 1 cm²/V·s limit. Figure 2 shows the state-of-the-art limits for mobility and on/off ratio for different techniques. What sets the mobility of a random network of semiconducting nanotubes in relationship to individual nanotubes? Can mobility be increased by increasing the density? How does this affect the on/off ratio, and what are the physical processes that set limits on this scaling? At the moment, no general theory exists which can answer these simple, but important, questions. Thus, even the simplest introductory question (what is the performance limit of semiconducting nanotube inks?) has not yet been answered quantitatively from first principles. This motivates a phenomenological approach and is the primary motivation for our publishing this review article. It is our hope that this will serve as a roadmap for the semiconductor industry as the technology gradually develops and moves from lab prototypes to commercial production.

**System Properties: Frequency Response.** Device mobility sets the current carrying capability and cutoff frequency. In long channel devices, cutoff frequency is proportional to the mobility of the device.

\[ f_t = \frac{\mu (V_{GS} - V_{th})}{2\pi L_{SD}^2} \]  

where \( f_t \) is the cutoff frequency, \( \mu \) represents the mobility of the device, \( V_{GS} \), \( V_{th} \), and \( L_{SD} \) are as defined above. Note that for short channel devices (which are not yet applicable in printed electronics) the cutoff frequency only depends on the electron drift velocity (saturation velocity) and is inversely related to \( L_g \). According to eq 8, it is advantageous to fabricate devices with very high mobility and short channel (gate) length. In radio frequency applications, power gain is also a critical figure of merit. An approximation of the frequency at which the power gain drops to unity (0 dB) is

\[ f_{max} \approx \frac{f_t}{2g_d(R_{ps} + R_g) + 2\pi f_tC_{pgd}R_g}^{1/2} \]  

where \( g_d \) is the drain conductance, \( R_{ps} \) and \( R_g \) are parasitic source and the gate resistances, respectively, and \( C_{pgd} \) is the parasitic gate–drain capacitance. As known, the presence of metallic nanotubes results in nonzero \( g_d \) which reduces \( f_{max} \). Therefore, the capability of depositing purified semiconducting nanotube networks is essential for RF applications, even more important than the mobility or on/off ratio, which are easier to model and measure, and so more often discussed in the literature. Although both

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**Figure 2.** Mobility and on/off ratio trend and comparison between different techniques for nanotransistors. From top to bottom: individual nanotubes show the highest mobility but are not scalable yet. Aligned SWNTs have low on/off ratio. Random networks are scalable, high on/off ratio with moderate mobility and also the advantage of operating in the saturation regime as desired for field effect transistors. Organic materials are alternative options with scalability and on/off ratio, but the state-of-the-art mobility is orders of magnitude lower than SWNT materials. The scale bar on the left shows the direction for increasing the mobility depending on the technique.
$f_{\text{max}}$ and $f_t$ are generally comparable in materials and devices with low $g_d$, they can be different by a factor of up to 100 in mixed SWNT networks\(^5\) and even graphene.\(^5\) Therefore, for practical applications, purified SWNT networks can have superior circuit performance even if the mobility is not as high as dense aligned arrays of SWNTs\(^5\) or even graphene.\(^5\) Recent work\(^5\) has achieved $f_t$, $f_{\text{max}}$ of 1–10 GHz using random networks of either purified or unpurified nanotubes, comparable to the best $f_t$, $f_{\text{max}}$ of dense aligned arrays\(^5\) and graphene.\(^5\)

**Deposition Technologies.** The prior section focused on theory of network electrical properties. In this section, we review the various techniques that have been developed to deposit such networks beginning with various nanotube semiconducting ink technologies. We use as our basis established processes for nanotube synthesis and purification discussed above. Our review first discusses the barest of inks, unpurified inks. Next, we discuss deposition of purified inks. Alignment techniques and purification techniques during and postdeposition are then reviewed. While the techniques are listed separately for clarity of exposition, in practice, many researchers demonstrate simultaneous application of more than one of the techniques discussed below in an attempt to improve overall performance.

**As-Grown Nanotube Inks.** By far, the simplest deposition technique involves deposition using inkjet or gravure printing techniques (Figure 3a,b), which result in completely randomly aligned nanotube networks. These techniques have the highest potential application in printed electronics, as they are extremely versatile and well-developed industries, with very high production capacity once the ink is provided. Heterogeneous integration on virtually any substrate is possible. Ink development for printed circuits requires a variety of sources (metal traces, dielectric insulator, semiconducting channel), and this review focuses on the use of carbon nanotubes for the semiconducting ink. By using various ink solutions, a variety of resultant electrical semiconducting material properties can be achieved.

The simplest inks consist of as-grown nanotubes, which (as discussed) typically consist of roughly 30% metallic tubes. This technique (first pioneered by Snow \textit{et al.}\(^4\)) demonstrated mobilities on the order of 10–100 cm$^2$/V-s, with on/off ratios on the order of...
techniques such as vacuum corresponding school of thought uses dry processing condition, the network is insulating. 46,64,66 However, due to the presence of metallic nanotubes, the on/off ratio is a challenge and has been given extensive attention, with attempts made to adjust the metallic nanotube density to be below the percolation threshold so that, in the off condition, the network is insulating.

While wet chemistry inks are the most versatile, a corresponding school of thought uses dry processing techniques such as vacuum filtration and stamping ("transfer printing"), which can result in similar networks of nanotubes. This is an alternative deposition technology with less flexibility in printing but more flexibility in integrating nanotube growth with the final network.46,64–66

Purification during Deposition. Amine-terminated surfaces have been shown to aid in nanotube adsorption.67,68 It has also been known for quite some time that amine moieties selectively bind to semiconducting nanotubes over metallic varieties.69 This concept can be exploited to achieve a quasi-purification effect while nanotubes are being deposited on APTES-functionalized surfaces.14,61,70 The resultant on/off ratio can be dramatically improved over and above that of unpurified nanotube networks, typically from ~10^2 to 10^5, using this technique alone. Mobility degradation does not seem to be an issue with this pretreatment technique. Investigations of various surface chemistries provide an opportunity for engineering of the electrical properties, with modest control of network mobility by the surface treatment recently demonstrated.16 However, it is fair to say that a comprehensive understanding of the effects of substrate material and surface chemistry on network properties is still a topic for future research, although to date (surprisingly), its effect seems to be rather modest.

Postdeposition Purification. Several techniques exist to remove metallic nanotubes postdeposition. Early attempts at purification included electrical breakdown of metallic nanotubes. Collins et al. from IBM utilized an electrical breakdown method to actually burn most of the metallic tubes in the channel.71 In their work, they fabricate devices from as-grown nanotubes. By applying an appropriate gate voltage, the semiconducting nanotubes can be gated off so that electrical burnout only destroys the metallic nanotubes. A potential drawback of this method is scalability as well as control over the process, although work by Motorola and Stanford has shown interesting reproducibility in this area.72,73 It should be noted that, while the on/off ratio is improved, there is usually a reduction in the ON current as well, sometimes over 2 orders of magnitude. The University of Central Florida has extended these studies in combination with dielectrophoresis (discussed below in the Alignment Methods section).74–76

Another approach consists of wet etching of metallic tubes. Generally speaking, this approach is based on the increased chemical reactivity of metallic nanotubes over semiconducting nanotubes, due to the increased density of electrons at the Fermi energy available for reaction chemistries (reviewed recently in refs 8 and 9). One of the early functionalization reagents used was diazonium to selectively react with metallic tubes.77–79 Using a controlled concentration of diazonium, it is possible to suppress the metallic nanotubes suspended in solution77 or after depositing them and fabricating TFTs.78 An on/off ratio of 10^5 was obtained using this method.78 Preferential metallic nanotube etching was achieved using a fluorine-based gas-phase reaction.80 Following on this theme, additional reaction chemistries involve cycloaddition reactions of nanotubes with fluorinated polyolefins.58 Electron-withdrawing nonfluorinated olefin chemistry is also effective via a 2–2 cycloaddition reaction.59

Stripe Method. Cutting the random nanotube network into narrow-width strips was demonstrated recently40,42 as an alternative to disrupt the metallic pathways from one electrode to another. Using conventional lithography and ion-etching technique, they are able to divide a channel of width W into thinner strips of width W_s along with the effective direction of charge transport. In this way, the metallic pathways through the channel will be discontinued along the etched regions, resulting in lower OFF current and higher on/off ratio. Although this technique will inversely affect the mobility, optimizing the strip width (W_s) can assist in maintaining the mobility.

Purified Nanotube Inks. Building on the deposition of mixtures, recent progress in purification technologies has led to the possibility of up to 99% semiconducting nanotubes (as determined by optical spectroscopic techniques) in solution (reviewed in refs 8 and 9). This has led to the demonstration of dramatically improved on/off ratios for a given mobility, recently demonstrated by several research groups.14,70,81–86

The effect of SWNT nanotube density can be and was systematically measured by us,14 which allows for the first time a controlled determination of the trade-off between all the electrical parameters in the material to be discussed further below.

Alignment Methods. It is generally the case that improving the alignment of the nanotubes in the network will provide some degree of improvement in the network mobility.59 Motivated by this effect, researchers have developed several techniques to affect alignment during deposition. To date, improvement in the mobility due to alignment has been modest and difficult to quantitatively assess, at the cost of extra processing. Whether this extra complication merits application in a commercial manufacturing environment remains to be seen.
By far, the simplest method to align during deposition involves spin-coating (Figure 3d). In this technique, radial orientation of the nanotubes is achieved. The wafer is simply coated as it spins, using techniques that are standard with the semiconductor processing industry. A drawback of this approach is the necessity to design devices and circuits with current flowing only in the radial direction. Similar flow-based alignment methods have been developed where the fluid flow direction can control the deposited nanotube alignment direction.

A more effective approach uses Langmuir–Blodgett troughs to achieve highly dense alignment. A subtle related effect (Figure 3c) uses the “coffee-ring” phenomenon. In this effect, as a solvent evaporates, the nanotubes are deposited preferentially along the edge of the bead of the solvent. This allows alignment along the bead edge, which can be engineered to form aligned arrays of nanotube stripes.

A final alignment technology which has received extensive attention in the literature uses ac electric fields to align nanotubes during deposition (Figure 3e). The effect (dubbed dielectrophoresis) is based on the time-averaged alignment force experience by a polarizable particle (or rod) in an ac electric field. This allows alignment along the bead edge, which can be engineered to form aligned arrays of nanotube stripes. One can calculate the sign of the dielectrophoretic force, which is usually repulsive for semiconducting nanotubes and attractive for metallic nanotubes. This tends to result in preferential deposition of metallic nanotubes. In principle, engineering of the surfactant and ac frequency may allow this issue to be addressed, although in practice, this has not been achieved.

One recent study has shown that, with a starting purified solution of 99% semiconducting nanotubes, the resultant network, although highly aligned, can end up with mostly semiconducting nanotubes deposited (>97%) and good on/off ratio (varying from 1 to 10^3, depending on the density); mobilities are ~1–10 cm^2/V·s. Another study used ultrahigh purity starting solution with trace amount of metallic nanotubes or less and achieved high on/off ratio (10^5) and a high degree of alignment, albeit without excellent mobility (2 cm^2/V·s). Thus, it seems that DEP alignment of all semiconducting nanotubes is feasible, although (to date) the mobilities are one to an order of magnitude below randomly aligned but purified inks, indicating that the relationship between alignment, mobility, and deposition process is not entirely understood. This could be because of the shorter source–drain spacing used in DEP-based experiments, which tends to (but does not always) result in lower measured mobilities (Figure 4b).

Roadmap for Applications: Phenomenological Nanotube Network Engineering. Above we presented theoretical models that are available for nanotube network properties as a function of materials parameters. Many of them are based on computational models and some on physical assumptions that are hard to test.
Therefore, we argue that a phenomenological approach is required to establish the field of nanotube network engineering. Below, we provide an overview summary of experimental work published to date, to establish trends, confirm models, and point out inconsistencies. Collectively, these observations lay a roadmap for future applications of nanotube semiconducting inks, including applications of existing technology, as well as avenues for potential improvements.

Scaling with Device Length. The mobility of a classical semiconductor is independent of its length. However, for nanotube networks, mobility is a more complex concept, as discussed in the theoretical section. In order to compare mobility from one device to another, the length of the device must be specified. As discussed in the introduction, the mobility according to the most sophisticated percolation-based theory should be inversely proportional to length. However, in practice, this is not always the case. The length dependence is not purely an alignment effect. For example, Figure 4a shows the length dependence of aligned arrays, which is increasing with length (possibly due to contact resistance effects). In addition, Figure 4b summarizes the state of the art of nanotube networks and includes data from three different laboratories, as well as both CVD-grown and purified SWNT inks. The results indicate that the length dependence typically observed is mild and is not explained by current theories. In summary, for the length dependence of the mobility:

- Experiments consistently observe length-dependent mobility
- Phenomenon not understood quantitatively or qualitatively
- No universal trend
- Not purely an alignment effect

Scaling with Density. The scaling of the critical performance parameters such as the mobility and on/off ratio has been studied mostly for CVD-grown nanotube networks, which are random with a fraction of metallic nanotubes. The effect of the density on the on/off ratio has been studied fairly carefully by only a few laboratories. Generally speaking, if the density of the metallic nanotubes is below the percolation threshold, but the density of semiconducting nanotubes is above the percolation threshold, then the on/off ratio can be quite large (Figure 5a shows SEM images of different densities). However, finding and tuning this transition for unpurified materials is very difficult because the window of parameter space is small. (The metallic density is only 2\times lower than the...
semiconducting density.) That transition was achieved only by two groups in the last year, Maryland\textsuperscript{45} and Ohno/Japan.\textsuperscript{46} Maryland made a detailed study of the density dependence of CVD-grown networks and found a sharp transition from low to high on/off ratio at a tube density of about $1/\mu m^2$, and their results are plotted in Figure 3b. Ohno's study was less systematic but found the transition at about $10/\mu m^2$ (using longer CVD-grown tubes), although density dependence of the on/off ratio was not reported.

In the case of purified semiconducting nanotube inks, one would expect the metallic nanotube fraction to be $10^{-8}$ smaller than the semiconducting fraction, so that it would be well below the percolation threshold at almost all tube densities. The density dependence of the on/off ratio of purified SWNT networks is plotted in Figure 5b.\textsuperscript{14} (Similar behavior is observed for DEP-aligned purified nanotubes vs linear density.\textsuperscript{46}) However, we found that the density dependence of the on/off ratio is less severe, for reasons that are currently not understood. The answer may be related to the average nanotube length; however, this issue is important to address with future experiments. At the very least, now it has been quantified allowing a roadmap to applications, if albeit a phenomenological roadmap.

Next, we discuss the effect of tube density on mobility. Although higher tube density will clearly give higher ON current, the effect on mobility is not so clear. In fact, classical semiconducting materials sometimes have lower mobility for higher density, in both 2D and 3D systems. Therefore, the effect of density on mobility should be investigated numerically based on simulations, and we are unaware of any general theory on the scaling between mobility and density. Again, in such a situation, in order to drive the technology forward, one must resort to phenomenological characterizations, as we have done. In Figure 5c, we plot the mobility versus density we recently studied. To our knowledge, this is the only such study to date of any nanotube network system. Our results clearly indicate a trend of increasing mobility with increasing density. (Again, similar behavior is observed for DEP-aligned purified nanotubes vs linear density.\textsuperscript{29}) However, as discussed above, this also leads to a decreasing on/off ratio. Therefore, the coupled effects of these two parameters give rise to a competition between mobility and on/off ratio. By tuning the density, the user can adjust the trade-off between these two parameters. Therefore, the quantitative trade-off is important to establish, which we discuss next.

To summarize regarding the density dependence, it is
• Recently quantified
• Not understood
• Severe impediment to technology, needing further study

On/Off Ratio versus Mobility. As discussed, by changing the density, the on/off ratio and the mobility both change. Therefore, one can map out (through a careful density-dependent study) the on/off ratio as a function of mobility. Unfortunately, there are many variables that also can affect the mobility, so it is difficult to compare one lab’s work to another from the literature. For this reason, a systematic study changing only the density changes (keeping all other variables constant) is the best way to establish trends. We have, in fact, recently performed such a study.14 Our experiments show a clear trend and also establish some of the highest mobilities for a given density ever reported. This illustrates the potential of purified semiconducting nanotube inks. Surprisingly, when the other limited data from other groups14,70,82–84 are compiled on the same plot, the trend becomes clear when plotted on the same graph (Figure 6, blue data points). Although all of the presented research works use purified nanotube inks, the purification method and percentage (ratio of metallic to semiconducting), deposition techniques (drop-dry, spin-coating, DEP, etc.), and fabrication steps vary from one to another, which should be considered, as well. When compiling similar data from nanotube inks made of unpurified nanotubes, a similar trend emerges, but with a much lower mobility for a given on/off ratio, as also seen in Figure 6 (red data points).

The next step is to determine if such a trend exists for CVD-grown nanotube networks40,43,45,46,81,99 and the answer is also yes (Figure 6, green data points), although the scatter of data is larger, as there are many more reported experiments on this older technology, with many more parameters changing from experiment to experiment, other than just the density. Note that researchers tend to quote the best on/off ratio and best mobility in one sentence, but in reality, they are not achieved simultaneously, so that the literature must be carefully read to compare different techniques. Nonetheless, the trend clearly shows a similar trend to the networks deposited from solution, which makes sense, as both result in a random network of 1/3 metallic 2/3 semi-nanotubes. A recent advance was achieved by Ohno46 of mobility at a given on/off ratio for unpurified nanotubes. Although they do not explain the reasons for the improved result in their paper, we speculate that the improvement may be due to the long nanotubes (10 μm), which results in higher mobilities for a given on—off ratio. This is clearly an avenue for improved ink chemistry, to be explored in the future. Thus, Figure 6 represents the collective knowledge to date of the relationship between mobility and on/off ratio for nanotube inks and forms an important roadmap for the future of the field.

As we have repeatedly emphasized, a clear and comprehensive, predictive theory for the electrical properties of nanotube networks does not exist. However, a trend can clearly be observed looking at the data from hundreds of researchers around the world, that the mobility versus on/off ratio is significantly improved for purified semiconducting nanotube ink, over and above that of mixtures. Thus, summarizing, the following main points:

• Density seems to be KEY ingredient
• Dependence not quantitatively predicted by theory
• Density can be engineered
• Uniformly shows purified inks improve mobility for a given on/off ratio
• Phenomenological roadmap for the industry exists and is subject to continuous improvement
• May improve with more fundamental materials studies

Prospects and Challenges. Performance Limits Can Be Improved by Ink Chemistry. At this point, we would like to speculate about routes and prospects for improved mobility and on/off ratios. It is clear from studies on dense aligned arrays of CVD-grown nanotubes that at least 10× improvement in mobility is, in principle, possible, from 100 to 1000 cm²/V·s, for nanotube networks. Whether this can be achieved with random arrays is unknown but not out of the question. Next, the purity of the ink seems to improve the overall mobility for a given on/off ratio, and so we speculate in Figure 6 that an improved ink purity will drive the blue curve up and to the right. How much further the curve can be driven, and how high the mobility can eventually reach, is currently uncertain and an important topic for further research. A clear possible route to improved mobility is to use longer SWNTs. This has been shown by recent work of both purified100 and CVD-grown46 networks where longer tubes gave substantially larger mobilities for a given on/off ratio. In ref 100, for example, a mobility of >100 cm²/V·s at 10⁵ on/off ratio was observed after selective gel-based removal of short nanotubes, a much higher mobility than other groups that use purified, but short SWNTs (Figure 6). Similarly, the mobility of CVD-grown tubes was dramatically improved by the same group46 for a given on/off ratio by using 10 μm long SWNTs, much longer than other researchers typically synthesize.

A critical component for manufacturing is the ink chemistry. While the studies of deposited nanotube networks have been reviewed and studied in depth, a critical problem in high-throughput manufacturing is the ink viscosity and especially drying time. For roll-to-roll printing, the drying time should be short enough to allow for high-speed printing. Most published
studies do not address this issue, but it is critical for industry to address for future printing technologies. A separate issue still to be completely investigated is the role of the substrate on electrical properties. For materials under consideration as flexible substrates (such as PET), to date, there has been little evidence of degradation in mobility as compared to SiO2 on silicon wafers. This is somewhat paradoxical, as the PET has surface roughness typically comparable to or larger than the nanotube diameter, whereas SiO2 is usually smooth. This needs further study but at present does not seem to be a major practical impediment to high-performance inks. Finally, the effect of the surfactant (and their removal) needed for aqueous solutions on the electronic properties of the deposited networks needs to be investigated. To date, only one such comprehensive study has been attempted (by our group),15 but more research is needed to completely quantify this critical link between the chemical and electronic properties of nanotubes.

Our vision for this needed emphasis is shown in Figure 1. Of all the ingredients and technologies that go into manufacturing nanotube network electronics, those that involve the ink chemistry are the least investigated and the most fruitful component of the supply chain to attack in terms of return on investment of improved performance and cost. Applications Will Be Decided by Cost Considerations. Yields Must Be Increased for SWNTs To Be Competitive. Organic materials are also used vastly for printed electronic circuits.11,102,103 The advantage of these materials is mechanical flexibility, ease of use, and compatibility with low-temperature processes and flexible substrates. However, the stability of these devices toward air, moisture, and light exposure needs further effort. In addition, the electrical performance of such devices requires improvement especially in terms of mobility. Although the organic field effect transistors show very high on/off ratio (more than $10^7$ in some cases), they suffer from very low mobilities on the order of $\sim 1 \text{ cm}^2/\text{V}\cdot\text{s}$.11,104 This low carrier mobility makes organic FETs unsuitable for some high-current, high-speed printed electronics applications. Apart from process compatibility and electrical performance, cost is a critical issue to be considered in applications. So far, nanotube-based devices cannot compete with organic transistors in cost, but performance is orders of magnitude higher. A detailed economic model that allows the cost performance trade-off to be analyzed is possible and important for commercial entities and engineering teams looking to apply the technology in the field.

High-Performance RF Devices Are a Low-Hanging Fruit. In previous sections, some demonstrations of solution-based nanotube circuits in dc and low frequency ($\sim 100 \text{ Hz}$) have been discussed. However, the intrinsic radio frequency characteristic of individual nanotubes has been analyzed, showing capability of exceeding THz frequencies.2,105 The full potential of solution-based random network of nanotubes for the applications in high-performance RF devices has not yet been demonstrated, although devices made from random networks in the 10 GHz range have already been demonstrated.51,54,55 The main issue for random networks of semiconducting nanotubes is the potential impact of the reduced mobility compared to individual tubes or aligned arrays. The very small channel lengths required to obtain high frequencies (see the frequency and channel length relation in the theoretical background section) is a critical milestone for available printing techniques. Although techniques for making printed circuits typically achieve resolutions (and hence gate lengths) of $\sim 10 \mu\text{m}$, the recent introduction of self-aligned techniques to the manufacture of printed circuits has allowed submicrometer gate lengths to be achieved, even in inkjet printed devices.106 Thus, high-performance RF devices are a clear potential application for purified nanotube inks.

System Technology Demonstrations. The first comprehensive system demonstration using carbon nanotube semiconducting inks was presented in 2010 and consisted of roll-to-roll printed RFID tag. This system included a printable antenna, rectifier, and ring oscillator ($\sim 100 \text{ Hz}$) on plastic foils and operating at 13.56 MHz as a 1-bit RF tag.60 The highest mobilities of the nanotubes used in that work are $\sim 5 \text{ cm}^2/\text{V}\cdot\text{s}$, at an on/off ratio of 100; the number of active TFTs is $\sim 10$. Because it is a roll-to-roll (gravure) printing process, throughput is high. A higher level of integrated circuit demonstrations with nanotube networks of higher mobility (and hence operation frequency) by about an order of magnitude ($80 \text{ cm}^2/\text{V}\cdot\text{s}$ and 1 kHz) was demonstrated with very high levels of integration ($\sim 10,000$ TFTs), allowing for demonstration of basic logic circuitry (inverter, NOR, NAND).40 Although a higher level of integration, several steps require lithography and so the throughput is not purely roll-to-roll. Besides, here they used as-grown SWNT material whereas in roll-to-roll printing process, purified ink was used. Therefore, there is clearly room for improvement in system demonstrations in the future.

Recent work has attempted to fabricate printed circuits using purified nanotube inks, and this has allowed for the demonstration of inverters, NAND gates, and ring oscillators on both polyimide and SiO2 substrates with $< 3 \text{ V}$ operation.83 The semiconducting carbon nanotube network and high capacitance ion gel gate dielectric is patterned by inkjet printing. In their work, they immerse the substrates in a 1 mM ethanol solution of hexadecanethiol (for polyimide substrates) or anthracene thiol (for SiO2 substrates) for 12 h (which is a long time for large-scale printed circuits) in order to make a self-assembled monolayer on the Au electrodes. Printing
was accomplished in ambient conditions using a commercially available aerosol jet printing system. The water-based SWNT ink was printed on the channel area with a printing speed of 3 mm/s (5 mm/s for low-coverage films). The measurements are also performed in vacuum due to sensitivity of the gel electrolyte (used as dielectric) to moisture. This provides system-level demonstration of purified semiconducting inks in circuits. Although several challenges remain, all three of these results indicate the potential of nanotube ink in a variety of circuits and systems.

CONCLUSION

Nanotube-based semiconducting ink has been demonstrated to be technically superior in terms of mobility to any other semiconducting ink. Combined with recent purification technologies to remove metallic nanotubes, the on/off ratio has been addressed with several techniques. On the basis of several studies, we have attempted to provide the first draft in this paper of a comprehensive technology roadmap that summarizes state-of-the-art performance that can be expected for different applications. In addition, the field is continuing to develop, and additional advances are announced often, so that this framework should be updated frequently, although the fundamentals laid out in this paper remain. Several system-level demonstrations have shown the potential application of semiconducting nanotube ink in circuits of increasing complexity and performance, while simultaneously addressing the issue of manufacturability.

The potential for improved performance and lower cost systems requires additional effort to realize the projected advantages in various applications. We have outlined many of the “choke points” in the supply chain, starting from the fundamental material synthesis and ending with the system properties. We have argued that, while all areas of this chain should be addressed, the ink chemistry and composition is the least explored technologically and the most fruitful avenue to attack to exploit the potential advantages of semiconducting nanotube inks. Once this has been addressed, future work will be required to find the appropriate points of insertion into existing and future system-level applications.

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REFERENCES AND NOTES


