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Single-walled carbon nanotube networks for flexible and printed electronics

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Abstract

Networks of single-walled carbon nanotubes (SWNTs) can be processed from solution and have excellent mechanical properties. They are highly flexible and stretchable. Depending on the type of nanotubes (semiconducting or metallic) they can be used as replacements for metal or transparent conductive oxide electrodes or as semiconducting layers for field-effect transistors (FETs) with high carrier mobilities. They are thus competitive alternatives to other solution-processable materials for flexible and printed electronics. This review introduces the basic properties of SWNTs, current methods for dispersion and separation of metallic and semiconducting SWNTs and techniques to deposit and pattern dense networks from dispersion. Recent examples of applications of carbon nanotubes as conductors and semiconductors in (opto- )electronic devices and integrated circuits will be discussed.

Keywords: carbon nanotubes, transistors, printed

1. Introduction

Among the various choices of materials for printed and flexible electronics, single-walled carbon nanotubes (SWNTs) are unique in the sense that they can be either metallic or semiconducting. Metallic SWNTs can withstand larger current densities than copper or aluminium [1] and their electrical conductivity is extremely high [2]. Semiconducting SWNTs are intrinsically ambipolar and show equal hole and electron mobilities depending on environmental conditions [3, 4]. Carrier mobilities in individual carbon nanotubes reach tens of thousands of cm² V⁻¹ s⁻¹ at room temperature [5, 6]. They are both highly flexible and strong [7]. Networks or thin films of SWNTs are extremely stretchable without noticeable changes in conductivity [8]. They are environmentally stable and durable, and can be processed from dispersions at low temperatures, which makes them suitable for printing on plastic substrates. Although the conductivities and carrier mobilities in SWNT networks, which are limited by nanotube–nanotube junctions are much lower than those in individual nanotubes, sheet resistances of less than 100 Ω/sq [9, 10] and effective mobilities of more than 100 cm² V⁻¹ s⁻¹ [11, 12] are achievable while maintaining high transparency. Thus, SWNTs seem to be the perfect choice for printable, flexible and stretchable electronics. Unfortunately, many of these favourable properties are not easily or simultaneously accessible. The fundamental problem that prevented SWNTs from reaching widespread use in electronics over the past decade was the fact that all methods for SWNT growth produce a statistical mixture of about 1/3 metallic and 2/3 semiconducting nanotubes with a variety of diameters and therefore electronic properties [13]. In order to be able to use SWNTs for either highly conductive electrodes or as semiconducting layers, it is necessary to separate the different types and create stable and reproducible inks/dispersions for further device processing. There has been tremendous progress in this field over the last few years [14–17]. At least for semiconducting SNWTs the purification problem seems to be solved and it is now possible to tap the full potential of solution-processed thin film carbon nanotube electronics. In this review we will describe current methods for dispersing and sorting semiconducting nanotubes as well as SWNT deposition and patterning techniques. We discuss the...
application of SWNT networks as conductors for electrodes and as semiconductors in field-effect transistors (FETs) for large area and printed electronics. Examples of integrated circuits based on SWNTs and novel SWNT light-emitting devices will illustrate the recent progress.

2. Brief carbon nanotube basics

SWNTs are conceptually viewed as rolled-up sheets of graphene, and their electronic properties can be derived from those of graphene with additional boundary conditions. Each nanotube can be described by its chiral vector $C_h = n \cdot a_1 + m \cdot a_2$ with $a_1 = (a\sqrt{3}/2, a/2)$ and $a_2 = (a\sqrt{3}/2, -a/2)$ as the unit vectors (see figure 1(a)) with the hexagonal lattice constant $a = 0.246$ nm of the graphene sheet. The chiral vector determines how the graphene sheet is rolled-up. Hence, the pair of indices $(n, m)$ is used to identify each SWNT species. The chiral angle and diameter of the nanotubes can be calculated directly from these values [18]. Nanotubes with $n = m$, e.g. $(6, 6)$, are called armchair nanotubes and those with $m = 0$, e.g. $(10, 0)$, are zigzag nanotubes. Both types are achiral, that is they have a mirror plane, while all other SWNTs are chiral (see figure 1(b)). An $(8, 4)$ SWNT is the mirror image of a $(4, 8)$ nanotube. This led to the somewhat confusing usage of the word ‘chiralities’ for all different species of nanotubes, that is, for nanotubes with different pairs of $n$ and $m$.

Due to the introduction of periodic boundary conditions for the wave functions of the infinite graphene sheet in the circumferential direction, the allowed wave vectors around the nanotube circumference are quantized, that is they can take only a set of discrete values. The electronic properties of SWNTs depend directly on their chiral vector. The simplest description follows the zone-folding approximation, which introduces so-called cutting lines for the allowed wave vector values that run across the reciprocal lattice of the graphene [19, 20]. When at least one cutting line goes through the $K$ or $K'$ point of the graphene the resulting nanotube is metallic. This is the case for all armchair nanotubes and for those with $(m-n)\text{mod}(3) = 0$. All other nanotubes with $(m-n)\text{mod}(3) = 1$ or 2 are semiconducting.

The selection of the possible states in $k$-space leads to the characteristic density of states (DOS) distribution of carbon nanotubes. It is dominated by sharp peaks, i.e. the van Hove singularities (see figure 1(c)), which are a key feature of the DOS of 1D conductors. This narrow distribution of occupied and unoccupied states is the origin of the characteristically narrow absorption and photoluminescence peaks of SWNTs [21] (see figure 2(a)). The energy differences between corresponding van Hove singularities (i.e. $E_{11}$, $E_{22}$ etc) scale with the inverse of the diameter. They are plotted in the Kataura plot [22, 23] versus diameter and sorted by type. This enables the identification of metallic and semiconducting nanotubes from absorption spectra or radial breathing modes in resonant Raman spectra if the diameter range of the nanotubes is known [24]. The $E_{11}$ transitions, or bandgaps, of semiconducting nanotubes (diameter 0.7–2 nm) range from about 1.1 eV to 0.4 eV (near-infrared), while the $E_{22}$ transitions are between 2.2 eV and 0.7 eV (visible to near-infrared). Semiconducting carbon nanotubes show excitonic photoluminescence in the near-infrared ($E_{11}$ transition), which can
be used to identify their species in photoluminescence excitation/emission maps [21]. An absorption spectrum and excitation–emission map of a sample of dispersed nanotubes that contains only five different types of semiconducting SWNTs is shown in figure 2.

3. Dispersion and sorting of carbon nanotubes

There are three major synthesis methods for producing SWNTs. The most common method is chemical vapour deposition with metallic catalyst particles such as iron or cobalt/molybdenum in the gas phase or on support materials (e.g. MgO). The carbon sources are, for example, CH₄, C₂H₄, ethanol or CO. Typical commercial processes like HipCO® [25] and CoMoCat® [26] produce SWNTs with relatively small diameters (0.7–1.2 nm). The CoMoCat® process is notable because it allows for preferential growth of the semiconducting (6, 5) and (7, 6) nanotubes, although some metallic nanotubes are still present. Another type of SWNT synthesis relies on the vapourization of carbon in an inert atmosphere by arc-discharge [27], laser ablation [28] or arc plasma jet [29]. These methods produce SWNTs with larger diameters usually in the range of 1–3 nm. Finally, the plasma torch method provides a comparable synthesis environment to the arc-discharge growth with high processing temperatures in the range of 1000–1200 °C [30, 31]. The high temperatures are created by a dc-driven or radio frequency-induced thermal plasma. Carbon containing precursor gases such as C₂H₄ are used in continuous flow together with metal catalysts like Fe, Co or Ni, or organometallic compounds like ferrocene or Fe (CO)₅. The plasma torch SWNT growth was developed into a highly economical process with large scale systems reaching outputs of several kilograms per day and high quality SWNTs with diameters of 1.2–1.6 nm.

These commercially available SWNTs come as raw powders containing SWNTs of various diameters and electronic type, some soot/amorphous carbon, and possibly metallic catalyst residue. For further processing the nanotubes must be dissolved or dispersed. Unfortunately, they are essentially insoluble in almost all organic solvents [32, 33]. The length of the nanotubes reduces the entropic gain from interacting with solvent molecules and the strong van der Waals forces between the SWNTs favour the formation of tight bundles. Nanotubes can be de-bundled through the application of strong shear forces, e.g. by sonication or mechanical milling, but they must be stabilized afterwards to prevent re-aggregation. This can be achieved in a number of ways that are well-known from other colloids. SWNTs can be stabilized in aqueous dispersions by surfactants or tensides. The surfactant molecules (e.g. sodiumdodecylsulphate (SDS) [34] or cholates [35]) form a micelle structure around the SWNTs with the hydrophobic tails pointing toward the nanotube and the ionic/hydrophilic headgroups toward the water. Another very efficient dispersing agent for SWNTs in water is single- or double-stranded DNA of any type [36, 37]. The interaction of the aromatic nucleotide bases with the nanotubes is strong and results in helical wrapping while the sugar-phosphate backbone creates a partially negative surface charge and thus electrostatic stabilization. After sonication or milling in the presence of the dispersing agent, the SWNT dispersions are centrifuged at high accelerations (usually above 200 000 g) to separate individualized SWNTs from bundles and other residues. Stable dispersions with high concentrations (few mg/ml) of individualized SWNTs can be obtained with surfactants or DNA, which is essential for creating printable SWNT inks. However, all of these dispersion processes are largely non-selective, and metallic and semiconducting SWNTs are dispersed in equal quantities.

The first attempts to separate SWNTs according to their metallicity or diameter were quite expensive and limited to very small amounts in the nanogram range, which severely limited their applicability [37–39]. The first efficient and scalable separation method was density gradient ultracentrifugation (DGU) of SWNTs that were dispersed in a mix of SDS and cholates. The separation relied on the different buoyant densities of the SWNTs including their surfactant
shell, which depend on the SWNT diameter but also its metallicity [40, 41]. A more recent approach is the use of classic gel-chromatography [42–45]. An agarose gel column is saturated with SWNTs dispersed in SDS, and a pure SDS solution is used as the eluent. The metallic nanotubes exhibit the weakest interaction with the agarose gel and are washed out first. Semiconducting nanotubes interact more strongly, depending on their diameter [46]. These differences can be enhanced by tuning the pH and temperature [47]. It is thus possible to create nearly single-species dispersions in a scalable and reproducible way. This accomplishment can be regarded as a true breakthrough in this field of research and enables a range of studies and applications that were impossible until then.

While gel-chromatography separates already dispersed SWNTs, it is also possible to start directly with the selective dispersion of only certain types of nanotubes. This is achieved by mixing the raw carbon nanotube powder with conjugated polymers in organic solvents such as toluene or xylene, as originally discovered by Nish et al [48]. Suitable conjugated polymers are polyfluorenes and polyfluorene copolymers [48–55], regio-regular polythiophenes [56, 57], and also polycarbazoles [58, 59]. All of these polymers preferentially disperse semiconducting SWNTs, although the degree of selectivity varies. During dispersion the SWNTs are wrapped by the polymer chains in order to maximize the π–π electron interaction of the polymer backbone and the nanotubes. The length of the alkyl-side-chains that make the polymers soluble in organic solvents determines to some degree the diameter of the preferentially stabilized carbon nanotubes. Longer side-chains lead to the dispersion of nanotubes with larger diameters [50, 56]. The yield and selectivity also depend on the solvent [60, 61] and the molecular weight of the polymer. Lower molecular weights increase the selectivity but decrease the yield of dispersion [62, 63]; a minimum chain length is required for effective dispersion [64]. The obtained concentrations of semiconducting SWNTs in polymer solution can vary from tens of ng/ml to hundreds of μg/ml. In all cases there is still a substantial amount of polymer in the dispersion, which helps to stabilize it. However, its presence would hinder charge transport in a film produced from such a dispersion, as the conjugated polymers exhibit orders of magnitude lower mobilities than the SWNTs. The majority of the unbound polymer can be removed by filtration of the dispersion and washing of the obtained SWNT film with a solvent. Alternatively, sedimentation of the nanotubes at ultrahigh centrifugation speeds (>250 000 g) creates a pellet that is recovered and rinsed with a clean solvent. The purified SWNTs can be redispersed in the pure solvent, e.g. toluene, and used for spincoating, drop-casting or printing. An elegant but synthetically more challenging route is the use of conjugated polymers that are degradable after the selection and dispersion step and can thus be removed easily and without residue [65–67]. A thorough overview of selective polymer dispersion has recently been given by Samanta et al [68].

4. Deposition of nanotube networks

A variety of techniques to deposit SWNTs from dispersion with different densities and degrees of alignment have been applied over the years. The most common lab technique for thin film deposition from solution, spincoating, requires quite high SWNT concentrations in order to obtain a reasonably dense surface coverage as shown in figure 3(a). Very often an adhesion promoter is used to increase coverage, such as 3-aminopropylriethoxy silane (APTES) [69–71] or poly-L-lysine [72, 73]. Due to the centripetal forces during spincoating and the drying effects at the edges of the sample, the nanotube distribution is not completely uniform. Interestingly, longer nanotubes appear to become more abundant at larger distances from the center of the sample [74]. Other methods for large area deposition of SWNTs from dispersion include immersing a substrate with an adhesion layer in a SWNT dispersion, followed by rinsing [75–78], dip-coating [79, 80], spray-coating [81, 82], and Mayer rod or blade-coating [83, 84]. The latter can lead to a partial alignment of the SWNTs, which reduces the sheet resistance.

In general, good nanotube alignment is desirable especially for semiconducting SWNT networks. An easy way to obtain well-aligned SWNTs between two electrodes is the application of an electric field during drop-casting of the nanotube dispersion. Both high frequency alternating fields [85–88] and large dc fields [89, 90] are suitable (see figure 3(b)). Low concentrations of SWNTs are sufficient as deposition only takes place between the electrodes, which also avoids post-deposition patterning. However, the uniformity of deposition depends critically on the dispersion quality and this technique is not scalable. Evaporation assembly techniques that rely on the lyotropic liquid crystalline properties of SWNT dispersions at high concentrations are slightly more suitable for alignment of nanotubes over large areas. Under controlled drying conditions, aligned thin stripes or films of nanotubes can be deposited from SWNT dispersion on semi-immersed substrates [91–94]. The nanotubes assemble parallel to the drying line and good linear SWNT densities (10–20 μm–1) with high degrees of alignment are achieved. Strong alignment and very high SWNT densities of up to 500 μm–1 can be obtained by applying the Langmuir–Schaefer method to compress nanotubes on a water surface before transfer [95].

For application in field-effect transistors and circuits most of the techniques described above require the post-deposition patterning of the SWNT films to reduce leakage currents and device cross-talk. This can be done by selective removal of SWNTs with oxygen plasma while other areas are protected, e.g. by photoresist. Nevertheless, as the purified source material is expensive, more frugal, additive deposition techniques, i.e. direct printing of SWNTs, are desirable. Printing methods that require high viscosity inks such as flexography (viscosity range 0.05–0.5 Pa s), gravure (0.01–0.2 Pa s), offset (5–100 Pa s) and screen printing (0.5–50 Pa s) [96] have so far been rarely reported in literature, although commercial sources for high viscosity (unsorted) SWNT inks exist. For type-sorted nanotube dispersions the necessary high SWNT
concentrations remain yet to be reached, and may not be economical. High resolution printing methods for low viscosity inks, such as inkjet printing (0.001–0.04 Pa·s) and aerosol jet printing (0.001–1 Pa·s) are much more suitable for the dilute carbon nanotube dispersions and have been applied numerous times to create devices and circuits [61, 97–109].

Many inks are water-based [101, 105] and the surfactants that stabilize the SWNT ink must be removed after printing by rinsing. At least on a lab scale, dispersions of surfactant-free SWNTs in organic solvents such as dimethylformamide (DMF) [98] or 1-cyclohexyl-2-pyrrolidone (CHP) [103] can be applied as well. Surface treatment (e.g. adhesion layers or UV-ozone treatment) and surface energy of the substrate also play an important role for printing of SWNTs [103, 108] and can be utilized to improve network density, alignment of the nanotubes or spatial resolution of the printing process [100, 110]. Once they are deposited, the strong adhesion of SWNTs to a suitable substrate allows for many layers of nanotubes to be printed on top of one another [101]. Thus, the density of SWNT networks can be tuned from just above the percolation threshold, for example for the channel of a transistor, to high density, for example, for injecting electrodes. Okimoto et al demonstrated the potential of this approach by fabricating all-carbon transistors using ink-jet printing of DMF-based SWNT dispersions [98].

Most of the mentioned deposition techniques, especially those that include slow drying processes and prior removal of dispersion stabilizers, will lead to SWNT bundles of various sizes. These may affect the transport properties of the networks [111]. In aligned networks thin bundles can improve the interconnectivity of the nanotubes, as the length of conformal contact between SWNTs is beneficial to charge transport along the bundle. However, thick and disordered bundles are likely to lead to non-uniform networks, limited overlap, insufficient electrostatic coupling in field-effect transistors and large barriers for charge transfer between bundles [112]. Additional carrier scattering that occurs in SWNT bundles [113] compared to pristine individual SWNTs reduces carrier mobility but is negligible compared to the junction-resistance [114] that dominates nanotube networks at least for channel lengths above 5 μm.

In comparison to other printable conducting and semiconducting materials such as PEDOT:PSS or conjugated polymers etc [115] carbon nanotube inks are more difficult to handle and their formulation and stabilization are critical. On the other hand, being able to print SWNT networks with different densities [98, 101] and of different types of carbon nanotubes offers the freedom to create devices with vastly different properties from the same material with excellent electronic and mechanical properties suitable for highly flexible, stretchable and transparent circuits.

5. SWNTs for electrodes

The high conductivity of metallic SWNTs, their low absorption cross section and mechanical flexibility have made carbon nanotubes a strong contender as a replacement for metals or transparent conductive oxides in flexible and stretchable electronics [116–118]. Early examples include the use of dense films of SWNTs as anodes in organic solar cells [119–122], light-emitting diodes [123, 124] and photodiodes [125]. For these applications it is not strictly necessary to use only metallic nanotubes if the films are dense enough. Doping with HNO₃ or SOCl₂ helps to increase the conductivity. Sheet resistances of a few hundred Ω/sq and less are readily achievable [80, 83, 126, 127]. However, in order to achieve higher transparency for similar sheet resistances, the semiconducting nanotubes should be removed [9]. The network conductance can be increased significantly when very long (several micrometers and longer) nanotubes are used in order to reduce the number of intertube junctions that exhibit resistances of hundreds of kΩ [114]. As most dispersion methods (ultrasonication/milling) cause more or less damage and shortening of the nanotubes [128], which decreases the conductivity of networks and composites, less damaging
methods are pursued. The dry deposition of nanotubes directly from growth in the gas phase onto filters and subsequent dry-transfer yields highly conductive and transparent networks as shown by Nasibulin et al [10]. A mild and scalable process to disperse carbon nanotubes without strong mechanical forces is their chemical reduction with sodium in liquid ammonia. The resulting nanotubide salt is soluble in dimethylsulfoxide and forms a nanotube ink that is stable at very high concentrations but is also highly air-sensitive [129]. After deposition, for example by spray coating or doctor-blading under inert atmosphere, the films are re-oxidized to the neutral species by exposure to dry air. Ostfeld et al demonstrated that for similar transparencies (80% at 550 nm) the sheet resistances of such films (about 60 Ω/sq) are lower compared to those produced by conventional SWNT dispersions in aqueous surfactant solutions (about 120 Ω/sq) [130]. Organic photovoltaic cells that were fabricated with these SWNT films and ITO as the transparent anode showed almost identical performance. It is evident that SWNT thin films have the potential to replace conducting oxides as materials for transparent electrodes, especially in areas where flexibility and stretchability are important. However, their relatively high cost and the question of uniformity over large areas, as well as possible hot-spots for leakage currents, must be addressed in the future.

Another interesting aspect for organic and flexible electronics is the application of carbon nanotubes as electrodes in organic field-effect transistors. Initially multi-walled and single-walled carbon nanotubes were added to conducting polymers such as PEDOT:PSS [132] and polyaniline [133] to increase the conductivity of these printable electrodes. Also, dense networks of SWNTs were used as injecting electrodes for both organic [134] and SWNT transistors [135, 136]. Schottky barriers and the resulting contact resistance between the semiconductor and the injecting electrode can be a limiting factor for the performance of organic FETs, in particular for n-type semiconductors that require low work function contacts [137]. Several studies have shown that SWNT electrodes or SWNT-decorated electrodes improve charge injection substantially and thus enhance device characteristics [134, 138–144]. Unlike other methods for increasing charge injection, such as modifying the work function of the injecting electrode, the enhancement of injection by carbon nanotubes is equal for holes and electrons. Figure 4 shows an example for the impact of carbon nanotubes on charge injection into organic semiconductors. Top-gate/bottom-contact transistors with the conjugated polymer F8BT as the semiconductor show ambipolar transport. However, due to the large mismatch of both HOMO and LUMO level (highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively) with the work function of gold, the contact resistance is very high and non-ohmic when standard gold electrodes are used [145]. Coating these electrodes with a thin film of SWNTs substantially improved both hole and electron injection and consequently led to almost ohmic contacts and higher overall source-drain currents [131]. The underlying mechanism of injection improvement seems to be the strong electric field enhancement by the one-dimensional carbon nanotubes. It is thus applicable to any organic semiconductor, and highlights the additional advantages of using SWNT electrodes in organic electronics.

An interesting combination of carbon nanotube networks and controlled modulation of charge carrier injection is used in vertical light-emitting field-effect transistors (VFET) as demonstrated by the Rinzler group [146–148]. Here a dense network of SWNTs is used as a semi-transparent, percolating source electrode separated by a thin dielectric layer from the gate electrode underneath. An organic semiconductor layer is sandwiched between the source electrode and a top drain electrode. The voltage applied to the gate electrode modulates the injection barrier between the source electrode and the organic semiconductor and enables switching behaviour, and thus an efficient combination of the drive transistor and the OLED in a display pixel [148]. This concept can also be applied to metallic mesh source electrodes [149, 150]. However, the nanotube network provides a nanoscale conducting mesh that is difficult to achieve by any other patterning method.

Figure 4. (a) Schematic illustration of a bottom-contact/top-gate polymer field-effect transistor with F8BT as the semiconductor. (b), (c) Ambipolar output characteristics of equivalent transistors with and without SWNT-coated gold electrodes [131].
6. SWNT networks as semiconductors

While metallic carbon nanotubes are interesting as transparent electrodes for organic photovoltaic cells, as shown above, semiconducting SWNTs can also be used directly as the light-absorbing donor layer in heterojunction solar cells. As shown in figure 2(a), SWNTs absorb light in the near-infrared, which is advantageous for utilizing the whole solar spectrum for power generation [151, 152]. Their high carrier mobilities also promise to enable fast charge separation and transport to the electrodes, which is crucial for efficient solar cells [153]. Often C60 or PCBM serve as the electron acceptor layer in such photovoltaic cells [151, 154–156]. Again the purity of the semiconducting nanotube network is important, as metallic nanotubes would simply quench excitons and thus lower the efficiency. Energy transfer and charge trapping within a mix of semiconducting SWNTs would also result in a loss of power conversion efficiency. Unfortunately so far the maximum efficiency obtained in such solar cells is only 2.48% [157]. Given the high cost of the nanotube source material and purification, combined with the limited efficiency even compared to non-optimized organic bulk heterojunction solar cells (e.g. poly(3-hexylthiophene) with PCBM [158]), SWNT solar cells might be of more academic interest in terms of energy transfer and charge separation rather than their application.

More promising is the utilization of carbon nanotubes in field-effect transistors and electronic circuits. Individual semiconducting carbon nanotubes have been shown to be applicable in high performance circuits that can operate at high frequencies [159]. The extremely high charge carrier mobilities of individual nanotubes and their excellent electrostatic properties that enabled the fabrication of low voltage, sub 10 nm gate length transistors [160] continue to drive research in this area, although the initial promise of SWNTs as the solution to Moore’s law [161] has not yet been fulfilled. For their application in printed and flexible electronics, however, the solution processability and flexibility of SWNT thin films instead of individual nanotubes combined with properties such as high carrier mobility and good on/off ratios will be most important.

For printed and flexible electronics, nanotubes will be used as random or semi-aligned networks, and transistor channel lengths will be large, i.e. a few micrometers or more. The density of nanotubes within the transistor channel must be at least above the percolation limit to allow for current flow. This limit depends on the length and alignment of the nanotubes. SWNT thin films can be modelled mathematically as a finite-sized tube percolation network with variable intertube coupling [162]. Ideally, densities are much higher than the percolation limit (>10 SWNT/μm) to ensure high on-conductance for a given channel width and length and thus high apparent mobility in a field-effect transistor. This becomes a problem when metallic nanotubes whose conductivity is not modulated by the gate field are still present. Depending on their percolation threshold, the off-currents of a given transistor can be very high [163] and can be reduced only slightly by ‘striping’ the SWNT film to disrupt the metallic pathways [164].

The problem of residual metallic nanotubes led to a well-known trade-off between high on-conductance or apparent carrier mobility and high on/off current ratios [69, 165]. This is visualized in figure 5 where the on/off ratios are plotted versus the measured mobilities for a selection of solution-processed SWNT transistors that were published over the last few years. For possible applications of nanotube transistors in active-matrix OLED displays, the lower boundary for field-effect mobilities is 5–10 cm² V⁻¹ s⁻¹ [166]. At the same time the on/off current ratio should be at least 10⁶ to avoid unnecessary power consumption and guarantee maximum brightness contrast for each pixel [167]. High on/off ratios (10⁵–10⁶) might be reached in SWNT network FETs despite the presence of residual metallic nanotubes but only for very sparse networks, which results in low on-conductances and low apparent mobilities (<1 cm² V⁻¹ s⁻¹) [168].

The on/off ratio can be improved for denser networks by increasing the channel length (>25 μm), thus making continuous metallic pathways less likely. This is demonstrated in figure 6 for random SWNT network transistors with long (40 μm) and short (5 μm) channel lengths and equal network densities with and without residual metallic SWNTs. For transistors with long channel lengths, the off-currents are almost the same, irrespective of the presence of metallic SWNTs. However, as the channel length decreases to 5 μm the residual metallic nanotubes can bridge the distance and the off-current increases by several orders of magnitude. For the transistor without metallic nanotubes, the off-current remains unchanged and only the on-current increases as expected [63]. Although longer channel lengths will give
good on/off current ratios and high apparent mobilities for networks that contain some metallic SWNTs, the on-currents are lower compared to shorter channels and the overall transistor area increases, which is unfavourable for display pixels with current-driven OLEDs.

Clearly, the best way to reach maximum on-currents and minimum off-currents in a nanotube network transistor is to remove all metallic nanotubes. That is, more than 99% of SWNTs within the network must be semiconducting. Novel SWNT sorting methods such as gel-chromatography and selective polymer dispersion (see above) have recently enabled such pure semiconducting SWNT inks and thus a range of transistors and circuits with high mobilities (>100 cm² V⁻¹ s⁻¹) and high on/off ratios (10⁶) even with submicrometer channel lengths were demonstrated [12, 176, 177].

The next question is, what type of semiconducting nanotube is best for FETs? The field-effect mobility of carbon nanotubes scales with the square of the diameter [5], thus large-diameter nanotubes would be preferable. However, their bandgap scales with the inverse of the diameter and has a direct impact on the off-current at least in short channel devices, so smaller diameter SWNTs with larger bandgaps would be better for higher on/off ratios [178]. Finally, the performance limiting factors are contact resistance [179] and tube–tube junctions [114, 180]. While the intertube junction resistance restricts the carrier transport within a dense network, the injection barriers at the metal contacts become limiting for shorter channels. As the channel resistance is reduced further and further, either by high nanotube densities or shorter channels, the contribution of the contact resistance increases. Even for moderately dense networks, the contact resistance can already be higher than the channel resistance [63]. A better understanding of charge injection into networks and charge transfer at nanotube junctions is necessary for further improvements in device performance.

As we have seen, the field-effect mobility of a semiconducting SWNT film is often cited as an important device parameter because it largely determines the switching speed and on-conductance of a transistor with a given geometry. In most cases, the carrier mobility in a field-effect transistor is calculated from the transconductance in the linear or saturation regime by taking into account the channel length L, width W, and the capacitance [181]. In a typical thin-film transistor the gate capacitance is based on the parallel plate capacitor model and calculated from the thickness and dielectric constant of the insulating layer. However, determining the effective capacitance for SWNT network devices is not as straightforward as for conventional thin film transistors. Due to the electrostatic coupling of the SWNTs with each other and thus screening of the gate field, in addition to the quantum capacitance of SWNTs (C_Q = 4.0 · 10⁻¹⁰ F m⁻¹) [182], the usual plate–plate capacitor model (C_PP) can drastically overestimate the effective capacitance C_eff. For the calculation of the effective capacitance in a given device, the linear density of the SWNTs Λ⁻¹, the SWNT radius R, the effective dielectric thickness t and the relative permittivity εr of the dielectric must be taken into account as derived by Cao et al [183]:

\[
C_{\text{eff}} = \Lambda_0^{-1} \cdot \left[ C_Q^{-1} + 1/2 \pi \varepsilon_0 \varepsilon_r \ln \left[ \Lambda_0/(R \pi \sinh(2\pi t/\Lambda_0)) \right] \right]^{-1}
\] (1)

The difference between the effective and the plate–plate capacitance is large for low network densities of carbon nanotubes, as shown in figure 7. But even for high SWNT densities it should not be neglected, especially when the gate dielectric is very thin. While the effective capacitance for a
nanotube network with a linear density of about 5–10 μm⁻¹ on a 300 nm thick SiO₂ dielectric is already very close to the calculated plate–plate capacitance, the same nanotube network on 50 nm of HfO₂ would result in an effective capacitance of only 20% to 40% of the Cₚₚ value and thus lead to a large underestimation of the field-effect mobility. This calculation also implies that for very low SWNT densities (<1 μm⁻³) decreasing the dielectric thickness much further, e.g. by using self-assembled monolayer dielectrics [177, 184, 185], will not increase the on-currents substantially. Thicker dielectrics may actually be more suitable in terms of device stability and breakdown voltages [135].

A serious problem of SWNT transistors has been their large current hysteresis and shift of threshold voltage, which would be a fatal deficiency for any application that requires bias stress stability, such as drive-transistors in OLED displays pixels [166]. For p-type SWNT transistors a large threshold shift toward negative voltages is observed when they are operated in air. This effect has been largely attributed to the presence of water on hydrophilic substrates (e.g. oxides) and oxygen, which creates electron traps [186]. These also suppress electron transport in SWNTs under ambient conditions [187, 188]. The hysteresis is reduced and electron transport might be observed after devices are annealed in vacuum, covered with hydrophobic polymers (e.g. fluoropolymers) [189–191] or encapsulated with hybrid polymer/oxide films (see figure 6) [63].

SWNTs are intrinsically ambipolar with equal hole and electron mobilities (as shown in figure 6) although under ambient conditions they show a predominantly p-type behaviour [192]. For complementary circuits it is advantageous to have transistors that are either purely n-type or p-type but not ambipolar. Ambipolarity would lead to large power dissipation, for example, in complementary-like inverters. In order to create purely n-type SWNT transistors, molecular doping techniques have been applied, using polyethylene imine [193], viologen [194], NADH [195] and other reducing agents [174, 196]. The long term stability of these chemical dopants, especially under ambient conditions, remains to be tested. More permanent electrostatic n-doping is provided by encapsulation of nanotubes with PECVD-SiNx, which contains fixed positive charges and results in robust n-type behaviour [197].

Overall, the device performance of SWNT network transistors has improved drastically over the last few years with field-effect mobilities and on/off ratios that are competitive with other solution-processable semiconductors. However, important parameters such as reproducibility, bias stress stability and control over doping still require further development.

7. Integrated circuits and applications

An impressive range of integrated circuits that use purified and sorted semiconducting carbon nanotubes has been demonstrated over the past few years. Transistors with good bias stress stability, high on/off ratios and high on-conductance might be used in OLED displays as switch and drive transistors in a simple 2T1C architecture [166, 167]. Here, the high carrier mobility of SWNT networks is a clear advantage over solution-processed organic semiconductors, which rarely reach carrier mobilities beyond 1–5 cm²V⁻¹s⁻¹ [198]. However, the sometimes still poor on/off ratios, threshold shifts under bias stress, and device-to-device variations for SWNT transistors are problematic. Nevertheless, several nanotube transistor driven single OLEDs [71, 78, 199, 200] and a small active-matrix display [201] were reported.

The requirements for transistors in active-matrix backplanes for sensing, e.g. pressure sensors or photodiode arrays, are less rigorous. Only one transistor is needed per pixel and the drive currents and bias stress are much lower. The inherent stretchability of SWNT networks is ideal for pressure sensing arrays that may need to be stretched over curved objects. Recent examples of backplanes based on SWNT FETs include flexible visible light/x-ray imagers [202], as well as conformal pressure and tactile sensor arrays [72, 203]. For such large area applications scalable and low-cost patterning methods are needed. Figure 8 shows the example of a 20×20 array of SWNT transistors that were patterned by gravure printing using silver nanoparticle ink for the electrodes and a barium titanate nanoparticle/poly(methyl methacrylate) composite for the gate dielectric [77]. The dielectric layer also served as an etch mask for the nanotubes, that were deposited by immersion of the PET substrate in a purified 99% semiconducting SWNT solution for two hours. The completed transistors showed mobilities of 4.3±1.6 cm²V⁻¹s⁻¹ and on/off ratios of 10⁴ to 10⁵. The device-to-device variability was relatively high but still impressive for such a simple and low cost printing and patterning technique. Similar results were obtained by screen-printing of the same materials [78].
Those printed transistor arrays on PET foil were flexible and bendable but not necessarily stretchable due to the mechanical limitations of the dielectric and the electrodes. In order to make full use of the excellent mechanical properties of SWNT networks, the other transistor components have to be optimized as well. A convenient way to enable stretchable SWNT transistors while maintaining high performance is the use of electrolyte-gating with soft or rubbery iongels [204, 205]. In an electrolyte-gated transistor the gate dielectric is replaced with an electrolyte, for example, an ionic liquid with a large electrochemical window [206]. When a gate voltage, and thus an electric field, is applied the anions and cations drift toward the gate electrode and the semiconductor, respectively, to form nm thick electric double layers. The applied gate voltage now drops across these thin double layers, which leads to very high effective capacitances on the order of $1–10 \mu F \text{cm}^{-2}$. Hence, very high charge carrier densities can be accumulated at low gate voltages ($<2$ V). High on-conductances and low operating voltages are feasible [199, 207]. For networks of carbon nanotubes, electrolyte-gating is especially efficient and avoids the problem of tube-to-tube screening as the ions accumulate around each nanotube. The effective capacitance is only limited by the quantum capacitance of the carbon nanotubes [182, 208, 209]. The main drawback of electrolyte-gating is the limitation of the switching speed by the movement of the ions in the electrolyte, although the maximum operating frequencies of electrolyte-gated SWNT transistors are still in the MHz range [106].

Iongels are printable and flexible and combine the high ionic mobility of ionic liquids with the mechanical stability of polymer gels. They have been shown to be highly suitable for various electrolyte-gated transistors [210–213] including SWNT transistors [105]. Xu et al used purified (7, 5) SWNT networks, pre-stretched buckled gold electrodes and an iongel to create highly stretchable transistors on a PDMS substrate [204]. The devices could be strained up to 18% before the on-currents started to drop. Further, combining metallic SWNT electrodes with semiconducting SWNT networks for metal-free all-carbon transistors could provide excellent flexibility and stretchability as well as transparency as recently demonstrated by Sun et al with dry-transferred CVD-grown SWNT networks [135].

While individual transistors can be used to study charge transport in solution-processed or printed SWNT networks, more complex circuit structures and more rigorous requirements on switching speed and device-to-device uniformity are necessary for future SWNT-based electronics. Basic integrated circuits have already been fabricated using solution-processed SWNT networks such as complementary inverters [63, 108, 174, 194, 197, 214, 215], ring-oscillators which consist of an uneven number of connected inverters [105, 106, 109, 191, 216, 217], NAND gates [174, 214, 218], NOR gates [109], D-Flip-Flops [219, 220] and others. These
circuits are the basis for even more complex devices such as RF-ID tags [221], static random access memories (SRAM) [135], shift registers, and so on. As one of the fundamental building blocks for integrated circuits, the inverter is a good example to illustrate the requirements and challenges for SWNT circuits. The most common inverter design is that of a complementary inverter consisting of an n-type and a p-type transistor in series and connected gate electrodes as the input node (see inset, figure 9). At a given low or high input voltage one transistor is on and the other is off. Consequently, the output voltage is high and close to the supply voltage ($V_{DD}$) or very low ($\sim 0$ V), respectively (see figure 9(b)). The on-currents and threshold voltages of the two transistors must be matched to obtain rail-to-rail operation, that is, full inversion of the input voltage. The complementary inverter design provides high gain and a large noise margin, which is essential for the successful integration of a large number of inverters. Power dissipation is low because current only flows at the inversion point (see figure 9(c)), that is, only for short periods of time.

Unfortunately, under ambient conditions SWNT network transistors exhibit mainly hole transport as mentioned above. In order to create stable n-type behaviour local doping is required (see above and figure 9) [194, 214]. An alternative to n-doping of the SWNT network is the incorporation of other solution-processable, high-mobility semiconductors such as zinc tin oxide for n-type transistors in combination with SWNT p-type transistors [222]. Good control over the threshold voltages is also needed in order to achieve voltage inversion ideally at half of the supply voltage. On/off ratios of the individual transistors must be high even at high source-drain voltages (i.e. supply voltage).

Ambipolar SWNT transistors can be employed to create complementary-like inverters that are usable for MHz ring-oscillators [63, 106, 109]. Here, only one semiconducting layer is necessary and under ideal conditions the hole and electron mobilities are equal. However, since none of the transistors can be fully off at any input voltage, the static current flow and thus power dissipation in ambipolar inverters is very high. Truly complementary SWNT inverters are superior in performance but require more processing, which may lead to device-to-device variations and patterning problems at higher integration densities.

Despite these challenges the fabrication of short channel (<200 nm) transistors with very dense and aligned semiconducting SWNT arrays from sorted dispersions exhibiting on-conductances of $197 \pm 38 \mu S \mu m^{-1}$ and on/off ratios of $10^5$ by Brady et al [176] has again strengthened the endeavour to create high-performance, low power SWNT thin-film electronics for a post-silicon era. For given parameters, SWNT transistors could indeed outperform silicon FinFETs in terms of energy consumption and speed [16]. The numerous examples of integrated SWNT thin film circuits and the recent demonstration of a rudimentary SWNT computer based on aligned chemical vapor deposition (CVD) grown SWNTs emphasize the high potential for future carbon nanotube electronics whose full realization has finally become tangible [223].

A novel and somewhat unusual application of semiconducting SWNTs is as nanoscale emitters in near-infrared light-emitting devices. Light emission from semiconducting SWNTs can originate either from the impact excitation of accelerated holes or electrons [224–226] or electron-hole recombination [91, 227, 228]. Unfortunately, SWNTs are not particularly good emitters. Their quantum efficiencies reach a few percent at best and depend somewhat on chirality [229]. This deficiency has been attributed to the high mobility of excitons along the nanotubes, which enables them to find quenching sites, such as the tube ends or other defects, very quickly [230, 231]. However, for a single nanotube species the photoluminescence line width at room temperature is very narrow ($\leq 40$ meV) [232] and directly determined by its chirality with some influence by the surrounding dielectric.

Figure 9. (a) Schematic illustration of an SWNT inverter with doped n-type (NMOS) and p-type (PMOS) transistors. (b) Voltage transfer curves (inset shows the circuit diagram of the inverter). (c) Power characteristics of the inverter during operation. (a) and (b) reprinted with permission from [214], copyright 2013, American Chemical Society.
Their emission wavelengths between 900 nm and 2000 nm make them interesting for biological imaging and as nanoscale light sources for on-chip optical communication.

So far, there have been no examples of light-emitting diodes based on s-SWNTs in a conventional vertical stack structure. It is, however, possible to create a p-i-n-junction in a single nanotube or an array of SWNTs by employing two oppositely biased gates in a transistor structure. A clear rectifying behaviour and light-emission can be observed that originates from electron–hole recombination. Due to the intrinsic ambipolar transport in un-doped SWNT networks the simultaneous accumulation of holes and electrons within the channel is also easily achieved with a single gate electrode. When the gate voltage is set between the source voltage (usually at ground, 0 V) and the drain voltage, the effective gate potential is positive with respect to one electrode and negative for the other. Thus, a hole and an electron accumulation layer form. The lateral extent of the two accumulation layers and hence their meeting point depends on the gate and drain voltages. The resulting narrow emission zone can be moved through the entire channel, as shown in figures 10(a) and (b), by simply changing the applied bias. This is a typical property of all ambipolar transistors based on emissive semiconductors such as conjugated polymers or quantum dots, and also works for a single carbon nanotube.

For ambipolar networks of different semiconducting nanotubes, the electroluminescence spectrum of such a light-emitting transistor exhibits emission peaks at the same wavelengths and with the same line width as the corresponding photoluminescence spectrum. However, the intensity distribution is shifted toward nanotubes with smaller bandgaps as shown in figure 10(d). Further, at very high charge carrier densities that can be achieved by electrolyte-gating the electroluminescence spectrum shows additional peaks that can be attributed to emission from charged excitons, i.e. trions.

Light-emitting SWNT devices based on impact excitation are usually unipolar and require high lateral electric fields to provide the necessary kinetic energy to create excitons. In order to keep voltages low the distance between the electrodes must be short (<1 μm), gate electrodes are not necessary if carrier injection is sufficient. Since the created excitons are not fully thermalized before photon emission the electroluminescence spectra of these devices are significantly broadened (peak width 100–200 meV). Due to the high excitation energies even E22 emission appears to be possible.

Although the emission efficiencies for both types of SWNT light-emitting devices are very low and reach 0.01% at maximum, the large current densities enable reasonable optical output and the emitted light is strongly polarized. The possibility to couple these planar and tuneable...
near-infrared emitters to waveguides [238] on a chip could lead to interesting applications of SWNTs beyond simple electronic circuits.

8. Conclusions

Over the last few years the field of solution-processed carbon nanotube electronics has made tremendous progress. One of the major problems that prevented the application of carbon nanotubes as semiconductors in printable and flexible electronics—the separation of metallic and semiconducting nanotubes—has finally been solved. Dispersions of purely semiconducting nanotubes can be produced economically on a large scale. This finally allows the numerous excellent properties of carbon nanotube networks to be utilized in large area, printed, flexible and stretchable electronic devices. Although there are still a number of challenges that need to be addressed, for example stable n-doping, bias stress stability, uniformity, etc, the opportunities of carbon nanotube-based devices are plentiful and many impressive examples already exist. In addition to the engineering task of creating functioning prototypes, future fundamental research could focus on the peculiarities of charge transport in networks of carbon nanotubes with different bandgaps and different densities beyond simple percolation theory. Long term performance stability under ambient conditions and the influence of bias and mechanical stress will be of interest, as well as light emission from SWNT networks. Overall, the field of carbon nanotube electronics has finally entered a phase where, thanks to the availability of pure and well-defined materials, much more reliable structure–property relationships can be investigated and exploited, and real-world applications become feasible.

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