

ELECTRONIC DEVICES

Nanotube arrays made to order

With the help of the Langmuir–Schaefer method, semiconducting carbon nanotubes can be forced into extremely dense arrays with an almost perfect parallel alignment that can be used to create high-performance transistors.

Hagen Klauk

Owing to their unique electronic properties, semiconducting single-walled carbon nanotubes are possibly the perfect channel material for field-effect transistors in flexible electronic applications such as flat-panel displays, sensor arrays and plastic circuits. They could perhaps even be used to create microprocessors or solid-state memory for high-performance computing. However, for such applications to become a reality a number of manufacturing issues first need to be resolved. Nanotubes are typically produced as a mixture of semiconducting and metallic tubes, and therefore methods are required to efficiently separate them. This issue has in essence been addressed through the use of the density-gradient ultracentrifugation technique^{1,2}. However, the semiconducting nanotubes also need to be precisely positioned on the device substrate. In the past, this problem has often been circumvented by dispersing the nanotubes randomly onto the substrate and then relying on either high-resolution microscopy to identify the location of individual tubes³ or on the spontaneous formation of percolation networks^{4,5}. But to maximize the current density, and allow nanotube transistors to be scaled to submicrometre dimensions, it is far more desirable to have numerous semiconducting nanotubes all aligned along the intended direction of current flow.

Arrays of perfectly aligned carbon nanotubes have been grown before on quartz wafers and then transferred to another substrate, on which transistors consisting of hundreds of perfectly aligned nanotubes could be fabricated⁶. Unfortunately, this method only provides a relatively low nanotube density of ~5 tubes per micrometre. (This density can be increased to a degree⁷, but it will still limit the width-normalized transistor current to about $20 \mu\text{A} \mu\text{m}^{-1}$.) Furthermore, these arrays contain both semiconducting and metallic nanotubes, which compromises the on/off current ratio of the transistors, especially for short gate-lengths. Writing in *Nature Nanotechnology*, Qing Cao and colleagues⁸ have now shown that the

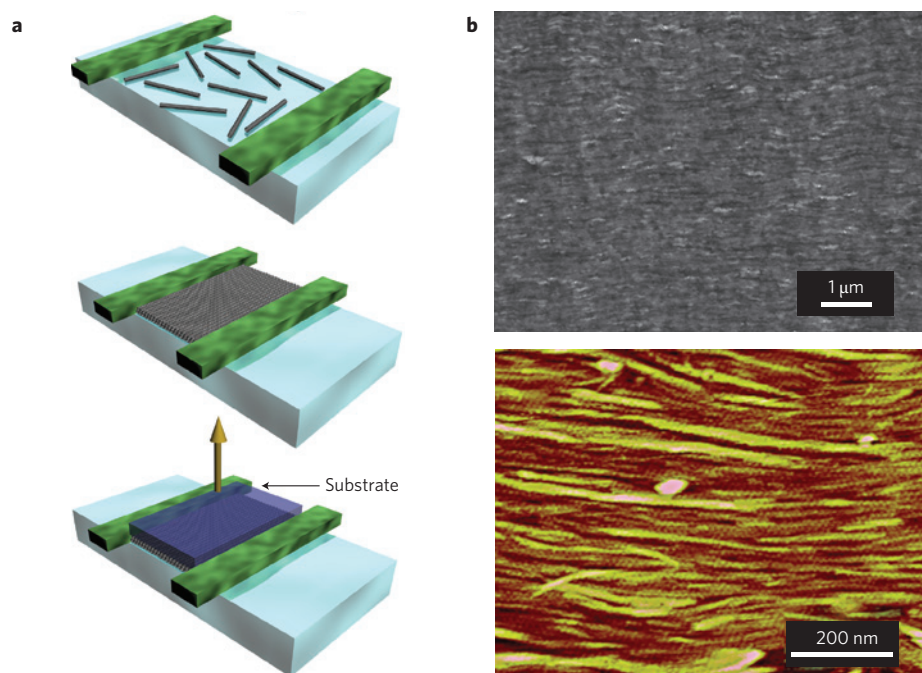


Figure 1 | Fabricating ultradense arrays of semiconducting carbon nanotubes⁸. **a**, Schematic of the Langmuir–Schaefer-based method for forming arrays of aligned nanotubes. The nanotubes are first sorted into semiconducting and metallic tubes using density-gradient ultracentrifugation. Semiconducting nanotubes are dispersed onto the surface of a water-filled trough and mobile bars (green) are used to compress the nanotubes into well-ordered arrays. The aligned nanotube arrays (or nanotube Langmuir film) can then be horizontally transferred (the Langmuir–Schaefer deposition) onto a solid substrate. These arrays can then be used to fabricate high-performance nanotube transistors. **b**, Scanning electron microscopy (top) and atomic force microscopy (bottom) images of the dense, aligned nanotube arrays on a silicon wafer.

Langmuir–Schaefer method can be used to create arrays of semiconducting single-walled carbon nanotubes with an almost perfect alignment and tube densities as high as 1,000 tubes per micrometre.

The researchers — who are based at the IBM T. J. Watson Research Centre in Yorktown Heights, New York — formed the arrays using a water-filled trough in which semiconducting carbon nanotubes are dispersed on the surface of the water. The nanotubes, which are pre-sorted with density-gradient ultracentrifugation, are compressed into a dense array using mobile bars that can be moved across the surface

of the water in a controlled manner. By measuring the surface pressure, the point at which the density of the compressed nanotube array reaches its maximum value before cracking can be identified. The array of aligned semiconducting carbon nanotubes is then transferred onto a solid substrate using a horizontal dipping method (the Langmuir–Schaefer deposition) and then used to create transistors (Fig. 1a). With the help of various microscopy and spectroscopy techniques, Cao and colleagues are able to quantify the degree to which the metallic nanotubes are eliminated by density-gradient ultracentrifugation (99% semiconducting, 1%

metallic) and the degree to which a parallel alignment of the nanotubes within the array is achieved ($\pm 17^\circ$).

Perhaps the most astonishing feature of this approach is the enormous nanotube density that can be obtained: the distance between adjacent nanotubes within the arrays is less than 5 Å and is apparently limited only by the van der Waals separation of the nanotubes (Fig. 1b). This nanotube density leads to very large current densities. For example, when the transistors have a gate length of 3 μm, which is larger than the average nanotube length, the width-normalized drive currents are as large as 4 μA μm⁻¹.

This current density may not seem that impressive when compared with low-temperature polycrystalline silicon thin-film transistors (TFTs), which are commonly used in active-matrix organic light-emitting diode displays and typically have drive currents of 50 μA μm⁻¹ when using similar gate lengths⁹. Or when compared with polycrystalline metal oxide TFTs, which are beginning to replace hydrogenated amorphous silicon TFTs in advanced active-matrix liquid-crystal displays and can have drive currents of 5 μA μm⁻¹ for a gate length of 20 μm (ref. 10). However, it is important to note that when the gate length

of a nanotube transistor exceeds the average nanotube length, the drive current is limited by the relatively inefficient charge transfer between the tubes.

A more revealing analysis is then perhaps to look at transistors in which the gate length is shorter than the average nanotube length. And indeed, for transistors with a gate length of 120 nm, Cao and colleagues have measured impressive drive currents of 100 μA μm⁻¹. This is within a factor of ten of the drive currents of state-of-the-art silicon metal-oxide-semiconductor field-effect transistors at the 22-nm technology node^{11,12}, despite the lack of contact doping in the nanotube transistors. Furthermore, respectable on/off current ratios of around 100 can be maintained in these devices when they are devoid of metallic impurities and composed exclusively of semiconducting nanotubes.

The encouraging performance of these devices invites the question — will carbon nanotubes ever replace silicon in microprocessors and memory? When posed to experts in industry, this question is typically met with responses that range from fervour ('absolutely') to a chuckle ('never'). The truth is that although the end of silicon has been predicted to be imminent for years,

silicon (shaped as fins or wires) is on track to meet the roadmap targets for the 14-nm and 10-nm nodes. But keeping up this pace has already led to the introduction of numerous exotic materials around the silicon channel (SiGe/SiC stressors, HfSiON/La₂O₃ gate dielectrics, TiN gates, NiSi/Cu contacts, SiBCN spacers). So beyond the 7-nm node, when the lithographic burdens will become almost unbearable, merely replacing those last few silicon atoms in the channel with carbon (whether in the form of tubes or ribbons) might actually be the least of Intel's and Samsung's worries. □

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MOLECULAR SPINTRONICS

Stretch for a moment

The spin of a single-molecule magnet is coupled to the vibrational motion of a single carbon nanotube.

Richard E. P. Winpenny

One of the aims of molecular electronics is to realize devices that make use of the quantum mechanical properties of a single molecule. The challenges are enormous however. For example, it is very difficult to control the location of a tiny object like a molecule. Also, it is necessary to design experiments that permit the reliable study of the physics of single molecules. Finally, and most importantly perhaps, the physics of a single molecule has to be linked to the design of devices intended for the macroscopic world.

Now writing in *Nature Nanotechnology*¹, Wernsdorfer and co-workers report on their experiment that links the magnetic spin of a single molecule with the vibrational modes of a carbon nanotube (CNT). Carbon nanotubes are already used as components of nanoelectromechanical systems due to their very high Young's modulus, which

gives them a remarkable stiffness for such a light element as carbon. The combination of stiffness and lightness has led to their use in ultrasensitive devices for ultrasensitive mass sensing^{2–4}, and for measuring magnetic behaviour of nano-objects⁵. Wernsdorfer and co-workers use a terbium single-molecule magnet (SMM) as the spin centre, and show that transport through the CNT is influenced by switching the spins of the terbium SMM firmly bound to it (Fig. 1a).

The terbium SMM is a derivative of the complex bis(phthalocyaninato)terbium(III) (TbPc₂) (ref. 6). Functionalization introduces a pyrene group that binds strongly to the surface of the CNT. The magnetic behaviour of TbPc₂ is due to a very well isolated doublet defined by the total angular momentum $J = 6$ with $J_z = \pm 6$. Terbium has a nuclear spin $I = 3/2$ and hence each state of the ground state

doublet is split into four states. In high magnetic fields, the TbPc₂ can only lose magnetization through a direct quantum tunnelling process $|J_z, I_z\rangle \rightarrow | -J_z, I_z\rangle$. As there are four possible values for I_z ($+3/2$, $+1/2$, $-1/2$, $-3/2$) there should be four such magnetization losses possible, separated by energy gaps due to the nuclear magnetic moment (Fig. 1b). Previously, this has been used to measure the nuclear spin of terbium directly by transport measurements through TbPc₂ (ref. 7).

In the experiment by Wernsdorfer and colleagues¹ the transport through a CNT shows four jumps in the differential conductance at specific external fields (Fig. 1c), corresponding to the nuclear spin states of the terbium. However, for these variations in conductance to occur, the nuclear spin of the terbium has to be somehow coupled to the nanotube. This is