ICT Module: 6.3

Graphene Device: Carbon nanotube transistor fabrication, CNT applications

Reference Book: James E. Morris, "Nanoelectronic Devices Applications Handbook", CRC Press

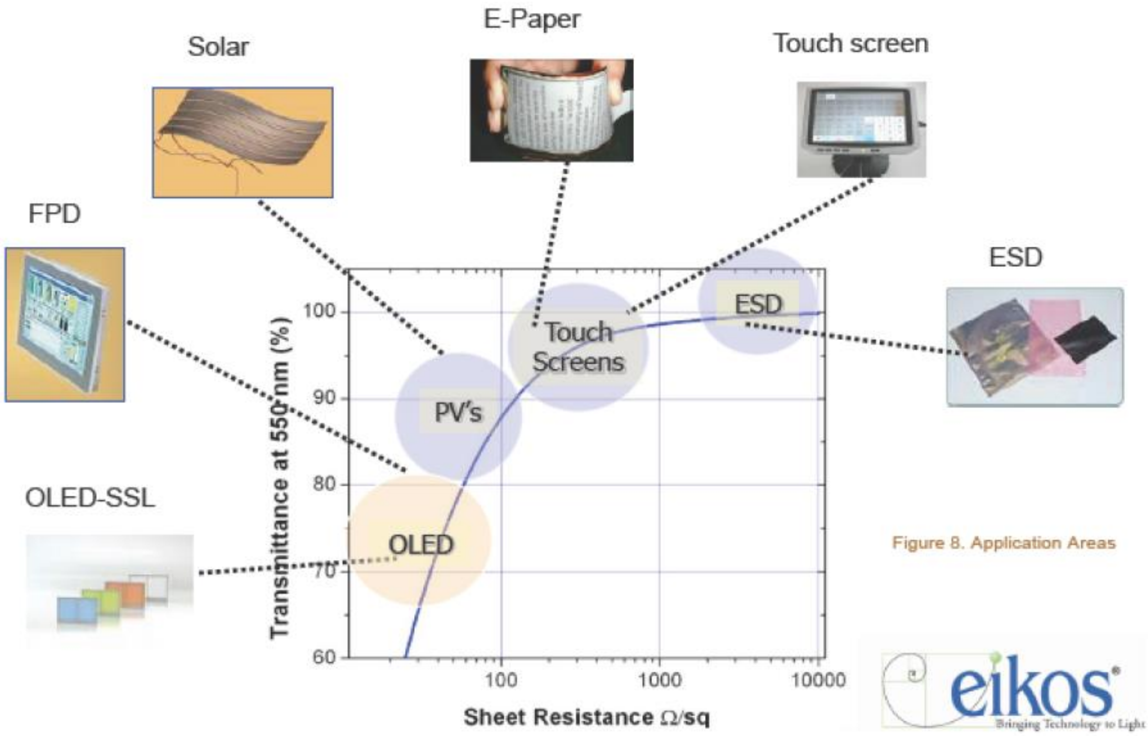
CNT Executive Features and summary

- Carbon nanotubes and graphene exhibit extraordinary electrical properties for organic materials, and have a huge potential in electrical and electronic applications such as sensors, microelectronic and semi-conductor devices, field emission displays (FEDs), nanoelectrodes and energy conversion devices (e.g., fuel cells and batteries).
- Carbon nanotubes are rod-like structures of carbon atoms. The strength and properties arise from the unique "rod" shapes. Indeed, applications cited include wires made of carbon nanotubes that are much stronger than steel for a given diameter.
- There are two types of carbon nanotubes – multi wall versions or single wall versions. It is the latter that are relevant to most electronics, offering metal-like conductivity from an organic material.

Key applications are transistors and conductors

- Depending on their chemical structure carbon nanotubes (CNTs) can be used as an alternative to organic semiconductors as well as conductors, but the cost is currently the greatest restraint.
- However, that has the ability to rapidly fall as applications grow and processing improves. Interest is high as CNTs have demonstrated to have carrier mobilities which are magnitudes higher than silicon, meaning that fast switching transistors can be fabricated.
- CNT will be able to provide high performing devices which can ultimately be made in low cost manufacturing processes over large areas. This is in contrast to polymer organic materials that many companies are developing for transistors, where the mobility is currently very low, severely restricting possible uses.
- While the fabrication of CNT transistors is still in early research phases, they are starting to be used for their conductivity properties, in addition to the fact that they can be **transparent, flexible** and **even stretchable**. In particular, they are being applied as conductive layers for the rapidly growing touch screen market. They are also likely to become a viable replacement for Indium Tin Oxide (ITO) transparent conductors.
- Conductive films will come first: In electronics, other than electromagnetic shielding, one of the first applications for CNTs will be transparent conductors. Here, applications are for displays, replacing ITO, touch screens, photovoltaics and display bus bars, connecting TFTs to the front plane, such as OLEDs. The following figure shows different applications and their requirements in terms of sheet resistance and optical wavelength transmittance.

Figure 1 Targeted applications for carbon nanotubes by Eikos



- **Transistors:** Possibly the most exciting prospect is for CNTs or graphene to be used to printed transistors that work at 50 GHz or more, outperforming the tradition silicon chip at much lower cost.

Introduction

First discovered by Sumio Iijima from NEC in 1991/92, and now a global focus of research and development, carbon nanotubes (CNT) are nanoscale materials that are highly attractive for electronic devices, energy storage devices, sensors and actuators.

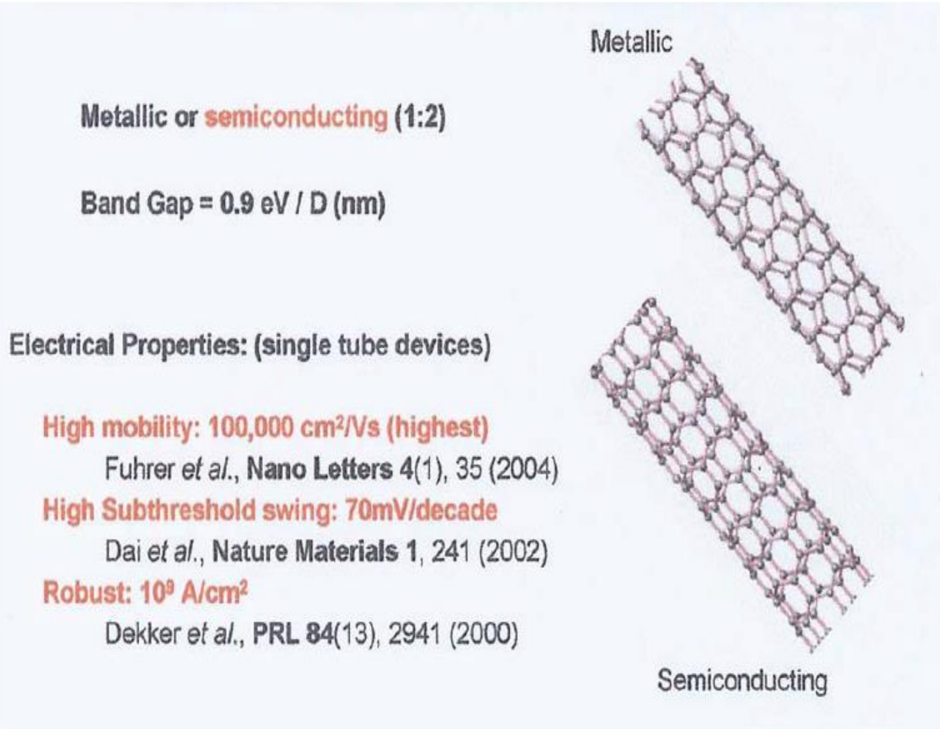
What are Carbon Nanotubes

Due to extraordinary mechanical, thermal and electrical properties and small size carbon nanotubes (also known as “bucky tubes”) have a huge potential in conventional and high technology electronic applications, such as sensors, microelectronic and other semi-conductor devices, field emission displays (FEDs), nanoelectrodes and energy conversion devices (e.g., fuel cells and batteries). Depending on the chemical structure they can act as metallic conductor or semiconductor, similar to silicon, appearing in the same group in the periodic table.

CNTs consist either of only one graphene layer (single-walled carbon nanotubes, SWCNTs) or multiple ones (multi-walled carbon nanotubes, MWCNTs) rolled in on themselves forming a tube

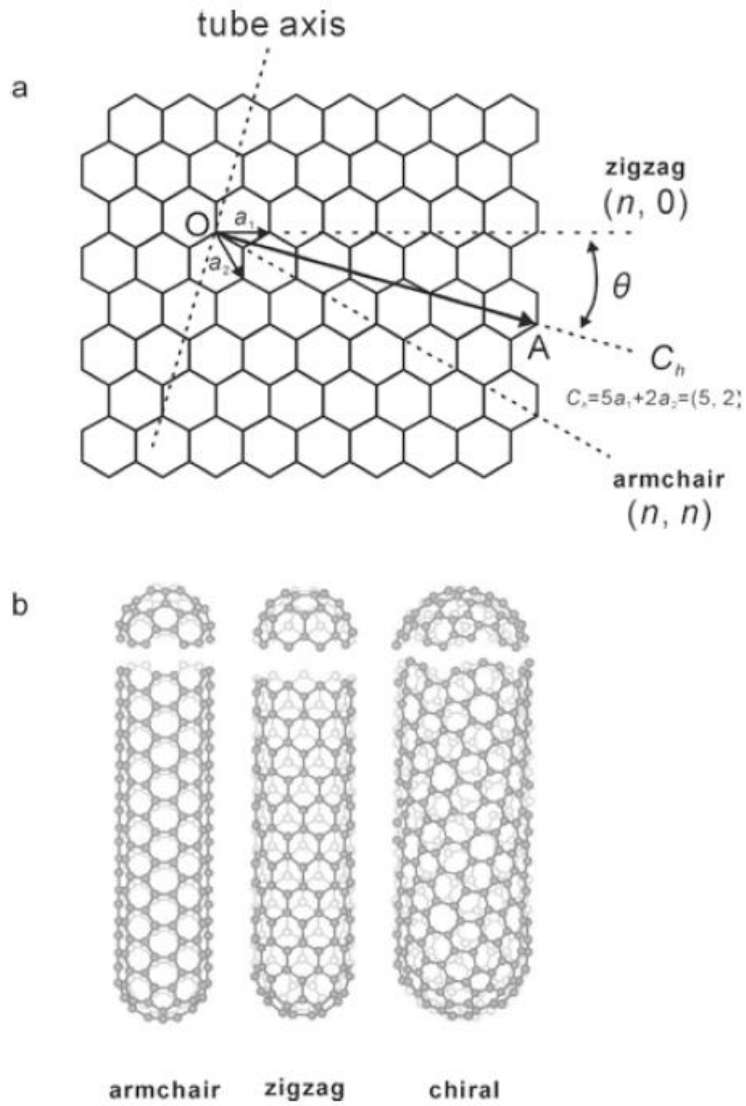
shape. They can range from less than a micrometer to several millimetres in length but are usually only a few nanometres wide, which is only a ten-thousandth the diameter of a human hair. The hollow, cylindrical tubes are composed entirely of carbon, like the members of the fullerene family; graphenes are planar sheets and the famous “buckyballs” are spherical fullerenes of 60 carbon atoms

Fig. 1.1 Structure of single-walled carbon nanotubes



The properties of CNTs, especially the electrical properties, are strongly dependent on the structure and the way the tubes are “wrapped up”. This is represented by what is called the chiral vector, which is a pair of indices (n, m) standing for the number of unit vectors along two directions in the crystal lattice of graphene. The formation m=0 is called "zigzag" and n=m is called "armchair". All other formations are referred to as "chiral".

Fig. 1.2 The chiral vector is represented by a pair of indices (n, m). T denotes the tube axis, and a1 and a2 are the unit vectors of graphene in real space



What is graphene?

- Graphene is being studied worldwide for electronics, displays, solar cells, sensors, and hydrogen storage.
- Graphene has a two-dimensional structure that looks like chicken wire and can be thought of as unrolled CNTs - it consists of a single planar layer of carbon atoms arranged in a honeycomb lattice. Graphene forms the basic structural element of some

carbon allotropes including graphite and carbon nanotubes. The surface area can be theoretically as high as around 2,600 m^2/g, but currently it reaches only 1,700 m^2/g in practice. Being 200 times stronger than steel, graphene is the **strongest known material.**

- Graphene is an ideal candidate for many high-speed computing applications in the multibillion dollar semiconductor device industry. Researchers found an electron moved at 1/300th the speed of light through graphene - potentially enabling terahertz computing, at processor speeds 100 to 1,000 times faster than silicon they claim.
- Graphene has extraordinary electron-transport properties; its monolayer thickness yields exquisite sensitivity to changes in environment, and its mechanical and thermal properties equal or exceed those of the best conventional materials.
- Nevertheless, one crucial issue remained – getting it to perform as a true semiconductor. The material lacks the ability to act as a switch. The University of Illinois found a way to overcome this mproblem by cutting nanoribbons in a special way so that they could be turned on and off.

Properties for electronic and electrical applications

- Looking closer, the huge potential of carbon nanotubes for electronic application derives in particular from their excellent mechanical strength, exceptionally high elastic properties, large elastic strain, low density, high thermal conductivity, and relative chemical inertness, not just superlative electrical properties
- The unique strength of CNTs arises from the chemical bonding of the carbon atoms similar to graphite. Between the individual carbon atoms covalent sp^2 bonds are formed, which results in extraordinary resilience and stiffness in terms of tensile strength and elastic modulus. In particular, single-walled carbon nanotubes are characterized by an outstanding electrical conductivity that MWCNTs cannot rival. Challenges arise in chemical complexity, reproducibility and purity regarding conductivity state, to name only some
- The tensile strength of CNTs is 60GPa and Young’s modulus is over 1TPa, which makes them asstiff as diamond. Typically they have an electrically conductivity of 10-6 Ohm/m and a thermal conductivity of 1750 to 5800 W/mK. Due to their covalent chemical bonds they do not undergo electro-migration or atomic diffusion, which has a positive effect on the current density being as high 4x109 A/cm2 – 1,000 times greater than copper.
- More important for the use in printed electronics are single-walled carbon nanotubes, because it is easier to control the shape and resulting properties of only one hallow tube than of multiple ones mrolled in on themselves as it is the case for MWCNTs. SWCNTs can have a diameter varying from 0.4 to 3 nm, are relatively stiff and outstandingly strong. This results in a high Young's modulus and high tensile strength.

CNT Key advantages in comparison to MOSFETs

- Better control over channel formation
- Better threshold voltage
- Better subthreshold slope
- High electron mobility
- High current density
- High transconductance

Comparison to MOSFETs

CNTFETs show different characteristics compared to MOSFETs in their performances. In a planar gate structure, the p-CNTFET produces ~1500 A/m of the on-current per unit width at a gate overdrive of 0.6 V while p-MOSFET produces ~500 A/m at the same gate voltage.[23] This on-current advantage comes from the high gate capacitance and improved channel transport. Since an effective gate capacitance per unit width of CNTFET is about double that of p-MOSFET, the compatibility with high- k gate dielectrics becomes a definite advantage for CNTFETs About twice higher carrier velocity of CNTFETs than MOSFETs comes from the increased mobility and the band structure. CNTFETs, in addition, have about four times higher transconductance The first sub-10 nanometer CNT transistor was made which outperformed the best competing silicon devices with more than four times the diameter-normalized current density (2.41 mA/µm) at an operating voltage of 0.5 V. The inverse sub threshold slope of the CNTFET was 94 mV/decade

Manufacture of CNTs

- Quite a few companies are already selling CNTs with metallic and semiconducting properties grown by several techniques in a commercial scale but mostly as raw material and in limited quantities.
- However, the selective and uniform large-scale production of CNTs with specific diameter, length and electrical properties is yet to be achieved. The coexistence of semiconducting and metallic CNTs after synthesis and the difficulty in separating them have been significant limitations for the use of carbon nanotubes in electronic applications. Lacking a method that reliably fabricates CNTs with the same structure and chirality, several separation methods have been discovered over the last years – mostly complex, time-consuming and expensive.
- **For all manufacturing processes** a hot transition metal based on nanoparticles is needed as a catalyst. Placed in contact with a carbon source in form of a gas, the latter one deposits carbon atoms that grow on the catalyst surface. The characteristics of the resulting CNTs, i.e. structure (single-walled or multi-walled), diameter and others, strongly depend on the diameter of the catalyst.

- The original synthesis method from 1991 was Arc Discharge, which was later followed by several other processes. Today, the main ones are Arc Discharge, Laser Ablation and Chemical Vapor Deposition (CVD). The last one is mainly used to produce multi-walled carbon nanotubes (MWCNTs). Synthesis processes allow the production of large quantities of CNTs but most of them need to take place in vacuums or with process gases. Recent advances, e.g. in catalysis and continuous growth processes, make carbon nanotubes more commercially viable.
- The synthetic techniques known for SWCNTs mostly generate significant quantities of impurities including amorphous carbon, residual metal catalyst and graphitic nanoparticles. There are currently three basic methods for separation, namely gas-phase, liquid-phase, and intercalation methods. However, purification procedures increase the production costs and by that limit the use in commercial applications.
- A great challenge remains the dispersion of CNTs. The two main procedures used are probe style and bath style ultrasonic systems. However, to make nanotubes more easily dispersible in most solvents, a functionalization step is needed. That means it is necessary to physically or chemically attach certain molecules, or functional groups, to their smooth sidewalls. To fabricate thin films of nanotubes using dispersions several methods such as filtration, spraying, self-assembly, and spin coating as well as printing methods of nanotube 'ink' have been developed.

Search in Google for easier Fabricating technique for CNT

CNT Fabrication techniques:

Arc Method

The discovery of the CNTs with arc discharge was more or less an accident. Sumio Iijima from NEC found multi-walled carbon nanotubes in the residue of an electrical arc discharge. Carbon nanotubes are self-assembling from the carbon vapor that is caused by an arc discharge between two carbon electrodes. Sometimes a catalyst is used. The yield of this method, which is around 30%, highly depends on the uniformity of the plasma arc and the temperature. Still, it is the most widely used method for the synthesis of both single-walled and multi-walled carbon nanotubes. However, it produces high impurities and requires further purification to separate the resulting complex mixture of components.

Laser Ablation Method

The laser ablation method was first developed in 1996 by Dr. Richard Smalley and co-workers at Rice University, USA. The procedure needs to take place in a high-temperature chamber containing inert gas. A pulsed laser vaporizing a graphite board with a following cooling of the vapor causes the carbon nanotubes to develop on the chamber surface. Using composite of graphite and metal catalyst particles, mainly single-walled carbon nanotubes can be produced at a yield of around 70% purity. The diameter of the SWCNTs can be determined by the reaction temperature. This process is more expensive than either Arc Discharge or CVD. However, it has been unclear how to scale up production. Additionally, laser ablation leads to the growth of highly tangled CNTs - issues that are not easy to deal with when it comes to fabrication of nanotube-device architectures for applications.

Chemical Vapor Deposition (CVD)

Chemical Vapor Deposition is a very common method for the commercial production of CNTs, because of the large amounts that can be formed. A substrate containing catalytic metal particles (nickel, cobalt, iron, or a combination) on the surface is heated to approximately 700°C inside a vacuum chamber, in which two types of gas are poured. The carbon-containing one passing over the metal particles causes the metal to separate and form carbon nanotubes. The size of those can be controlled by the size of the metal particles. Carbon nanotubes can also grown directly on a substrate using a CVD process where the catalyst is first deposited on the substrate. Fujitsu is a leading manufacturer of CNTs grown directly on the substrate.

Printing Carbon Nanotubes

In order to get a printable dispersion from raw CNT powder produced with the mentioned processes above, the carbon nanotubes need to be functionalized by physically or chemically attaching certain molecules, or functional groups, to their smooth sidewalls. After this the tubes are dissolvable or dispersible in most organic or inorganic solvents.

Traditional printing methods are already used by Eikos and Unidym, to name a few. Nevertheless, using these traditional methods for the fabrication of thin carbon nanotube films there are still some hurdles to overcome. At the beginning there is the relatively poor quality of the nanotube starting material, which mostly shows a low crystallinity, low purity and high bundling. Subsequently, purifying the raw material without significantly degrading the quality is difficult. Furthermore it is still an issue to achieve good dispersions in solution and to remove the deployed surfactants from the deposited films.

Given these issues and additional steps needed after the manufacture of the raw material, the final CNT films are still costly to produce and have high sheet resistance for a given transparency. However approximately 90% of the costs for product films are due to post processing, which does not include the CNT material cost.

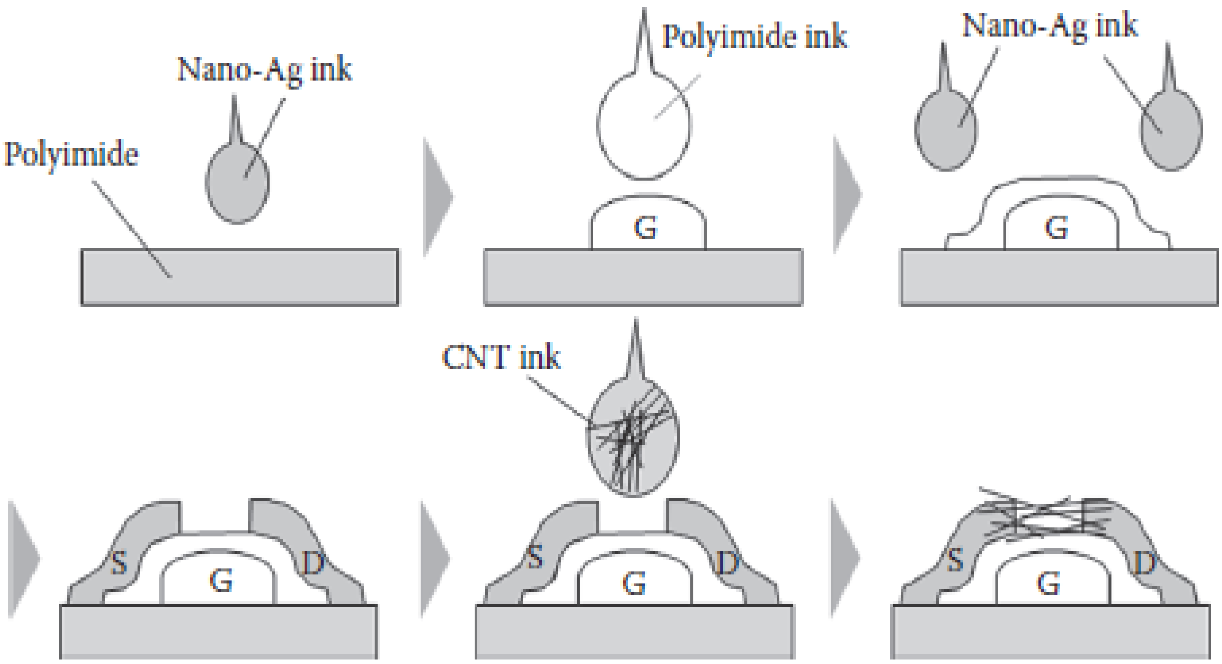
PRINTING FABRICATION TECHNOLOGY

Device Fabrication Flow

Device fabrication flow is shown in Figure below. All device elements were patterned by maskless printing methods with a minimum of materials.

- First, gate electrodes were printed on a polyimide (PI) film by use of an inkjet printer with nano-Ag ink (NPS-J, Harima Chemicals) and sintered in air.

- Next, gate insulators were formed by an ink dispenser with PI ink (CT4112, Kyocera Chemical)



Print fabrication flow.

In this fabrication process, all device geometries were defined by printing methods without an additional patterning process. Therefore, it is important to control the wettability between the material inks and the underlying surfaces.
In addition, there are two keys in the fabrication process. One is the reliability and uniformity of the printed gate insulators in order to successfully form such layered device structures. The other is the homogeneous dispersion of the CNT networks to improve device quality and performance.

CNT applications

1. Application of printed carbon nanotubes to flexible Displays

CNTs are flexible, highly conductive and transparent, making them of particular interest for display applications. In early 2009, after further investigations, the University of Tokyo presented Organic Light Emitting Diodes (OLEDs) incorporating their CNT conductor. The CNT conductor was used for the wire grid connecting the Organic Thin Film Transistors (OTFTs) and the OLEDs of the flexible display. They were screen printed 100-micrometer-wide lines. In the first project step the flexible conductive material was used to connect organic transistors in a stretchable electronic circuit. It was then used to connect organic light-emitting diodes (OLEDs) with the organic transistors addressing each OLED pixel. With improved conductivity and stretchability it is now possible to fold the display in half or even crumple it up without damage, and to stretch it up to 50 percent of the original shape.

The main hurdle for CNT based displays over the last years has been the lack of a big enoughsupply of semiconducting carbon nanotubes.

2. Application of printed carbon nanotubes to transistors

In February 2009 NEC Corporation, Japan, announced the successful realization of a CNT transistor on plastic film that is completely printed incorporating an advanced low-temperature printing process. All components of the CNT transistor – electrodes, insulator and CNT channels – are printed on a plastic substrate, which could be used due to production temperatures below 200°C. All materials used were optimized in order to keep interference between the layers low and to maintain printing conditions. The developed transistors demonstrate p-type conduction and an on/off ratio of 1,000. This is insufficient for managing grey levels in an active matrix display but adequate for general electronics.

3. Application of printed carbon nanotubes to energy storage devices – supercapacitors

Another group is working on using printable CNTs in energy storage devices. The gel electrolyte of the high-performance energy-storage device is sandwiched between two CNT electrodes. These were fabricated by spraying water-soluble CNTs onto a plastic substrate. This production step could also be done with existing inkjet printing technologies. After the evaporation of the contained water the result is a 0.6 micron thick randomly entangled CNT layer. The supercapacitor device stores energy at the surface of the carbon nanotubes when a voltage is applied to the sandwiched electrolyte gel

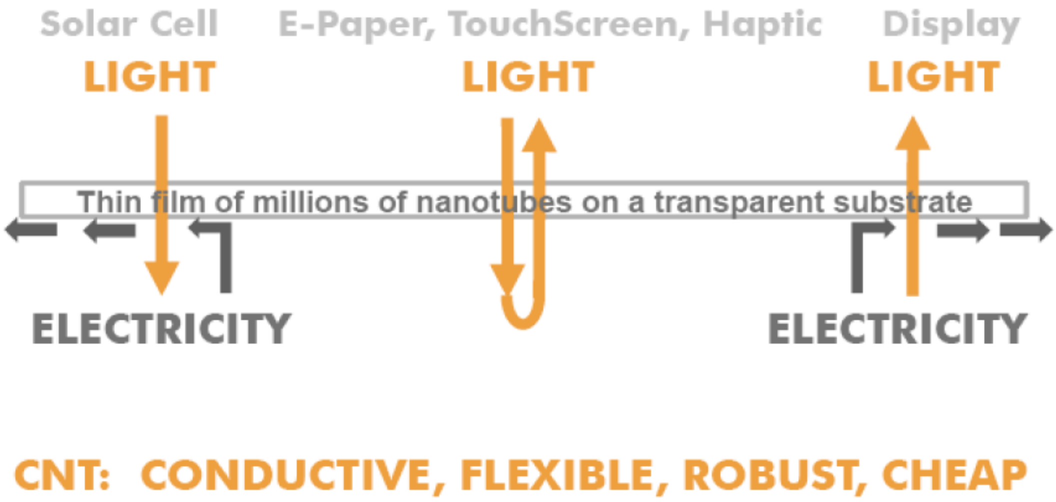
4. Carbon Nanotubes as conductors

With the right chiral vector (n=m) carbon nanotubes exhibit metallic properties. In theory, metallic nanotubes (n=m) can carry an electrical current density of 4×109 A/cm2. The promises of nanotube conductors are low cost, high performance, long life/durability, simple patterning, environmental friendliness, flexibility and transparency. Some of these benefits will allow CNTs to replace existing conductors but it will also enable new applications.

Fabricated as transparent conductive films, conductive carbon nanotubes can potentially be used as a highly conductive, transparent and cost efficient alternative to ITO (Indium tin oxide) for the use in flexible displays, for instance.

CNTs may offer a viable and even improved replacement for indium and gallium in many applications, including ITO.

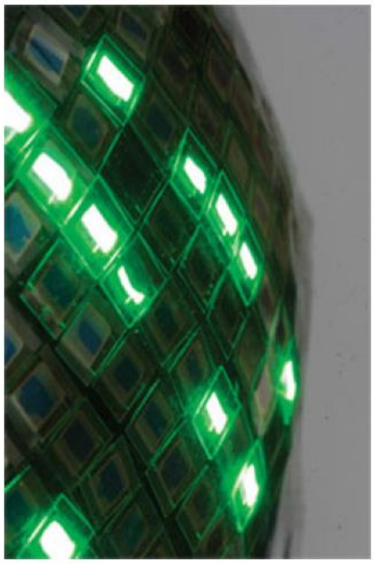
Fig. Potential applications are flexible solar cells, displays and touch screens.



a) CNT based conductor application in OLEDs

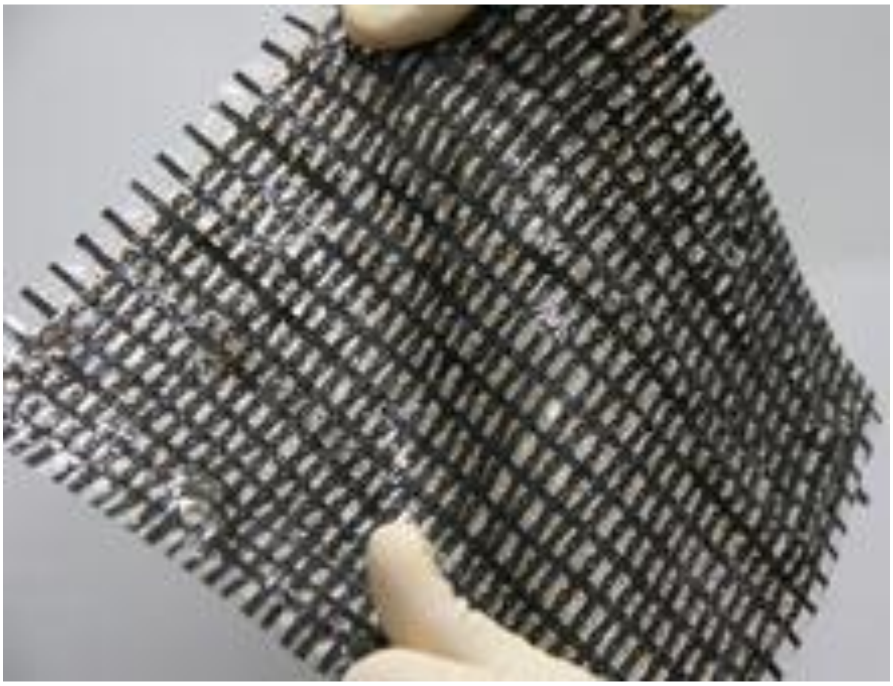
The flexible CNT-based conductor is now used to connect organic light-emitting diodes (OLEDs) with the organic transistors addressing each OLED pixel. With improved conductivity and stretchability it is now possible to fold the display in half or even crumple it up without damage, and to stretch it up to 50 percent of the original shape. Such durability means that this can also be applied in many other applications such as flexible actuators, sensing “skin” etc.

Fig. New printable elastic conductors made of carbon nanotubes are used to connect OLEDs in a stretchable display that can be spread over a curved surface



Source Takao Someya, the University of Tokyo

b) Stretchable mesh of transistors connected by elastic conductors

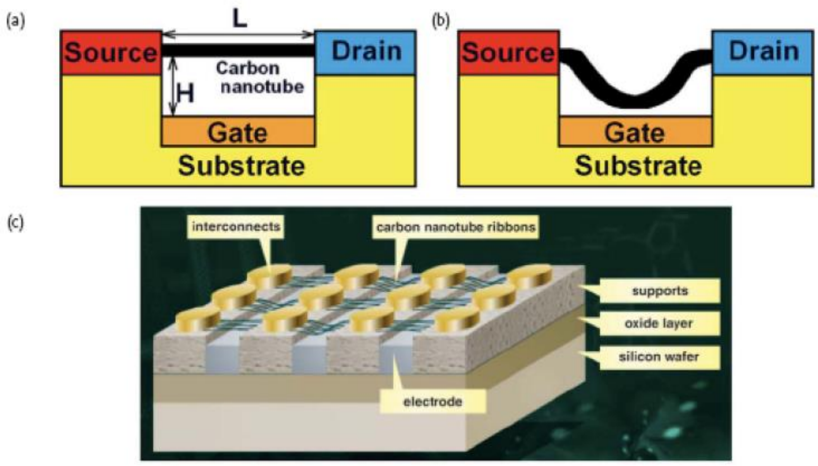


Other applications of CNTs

1. NRAM data storage device

In June 2008 the University of Nottingham, UK, in collaboration with Nantero Inc., USA, presented a carbon-nanotube-based electromechanical data storage device. The high-density nanotube-based non-volatile random access memory (NRAM) device was fabricated incorporating suspended, single or multiwalled CNTs. A bundle of these was suspended across a gap and connected to the two source and drain electrodes, as shown in the figure below. By applying a voltage the nanotubes is forced to flex and to come into van der Waals contact with the gate. This switches the device into the state ‘1’. This bent position is maintained until an applied pull-out voltage forces the nanotube to stretch back in the ‘0’ state.

Fig. A three-terminal memory cell based on suspended carbon nanotubes: (a) nonconducting state ‘0’, (b) conducting state ‘1’, and (c) Nantero’s NRAM™.



2. Organic photovoltaic devices and hybrid organic-inorganic photovoltaics

Hybrid organic-inorganic photovoltaics

The research and development organization Georgia Tech Research Institute (GTRI), USA, also presented its work on carbon nanotubes for more efficient solar cells. The GTRI photovoltaic cells trap light between their tower structures, which are about 100 microns tall, 40 microns by 40 microns square, 10 microns apart and built from arrays containing millions of vertically-aligned carbon nanotubes. Conventional flat solar cells reflect a significant portion of the light that strikes them, reducing the amount of energy they absorb. The carbon nanotube arrays serve both as support for the 3D arrays and as a conductor connecting the photovoltaic materials to the silicon wafer. The new cells remain efficient even when the sun is not directly overhead because the tower structures can trap and absorb light received from many different angles.

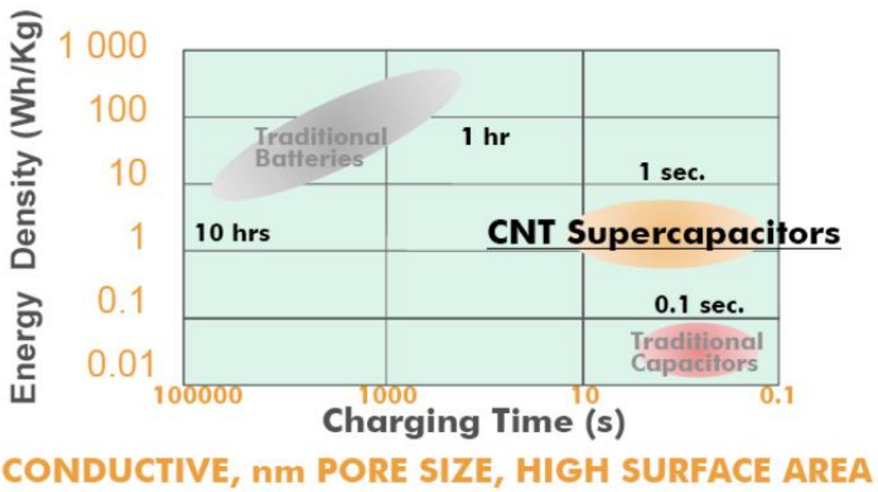
3. Application to Infrared solar cells

One major application is the infrared solar cells, where transparent CNT films as well grapheme films would allow the transmission of infrared energy to the active layer, which allows the fabrication of infrared solar cells. The fabricated films could also be used for other applications like an infrared camera, which will be investigated soon by the researchers.

4. Supercapacitors and/or batteries

Apart from the good electrical conductivity, the extremely high surface area of CNTs make them a very good choice for electrodes in batteries and capacitors. CNTs have the highest reversible capacity of any carbon material, as shown in the following figure. Batteries have a high energy density but are slow to recharge, where as capacitors have the opposite problem. CNT based supercapacitors are being developed to bridge the gap. There are huge requirements for this in energy harvesting devices for small electronics, such as wireless sensors.

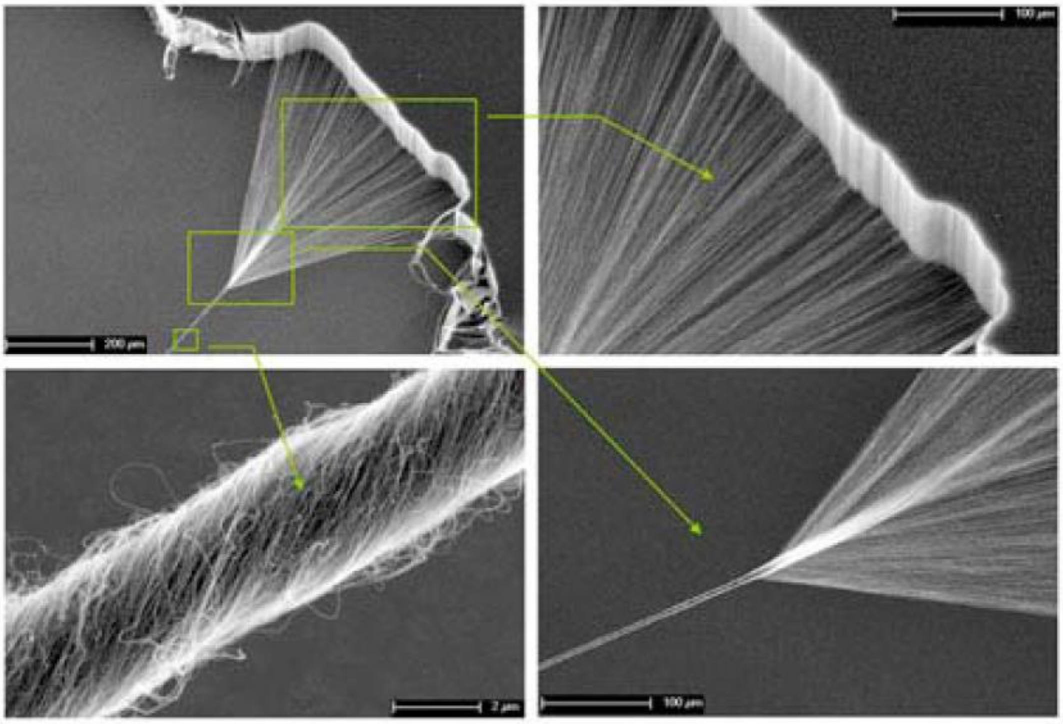
Fig. The carbon nanotube supercapacitor versus batteries and traditional capacitors



5. CNTs for smart textiles

For smart textiles carbon nanotubes are attractive in form of spun fibres along with CNT composite fibers. The advantageous properties are their flexibility while being super-strong and electrical conductivity. Potential applications are for example body and vehicle armor, transmission line cables, woven fabrics and textiles, flexible photovoltaics and displays in fabric etc. In addition the CNT-yarns, extruded fibers from CNT-blended polymers are studied regarding production process and properties.

Fig. Four scanning electron microscope images of the spinning of carbon nanotube fibres



6. CNT applications in Thin film loudspeakers

In September 2008 Tsinghua University, China, and Beijing Normal University, China, presented their collaborational work on flexible, stretchable, transparent thin film loudspeakers that incorporate CNT nano-ribbons. This device sounds roughly 260 times louder than that which can be produced from platinum foils. Applying an audio signal to the CNT thin film loudspeaker through a pair of electrodes causes the film's temperature to briefly spike and by that the directly surrounding air to oscillate, which produces sound waves.

Fig. The CNT thin film was put on a flag to make a flexible flag loudspeaker

Source Tsinghua University, China, and Beijing Normal University, China

The figure below shows a carbon nanotube thin film loudspeaker. (a) The CNT thin film was pulled out from a super-aligned CNT array grown on a 4 inch silicon wafer and put on two electrodes of a frame to make a loudspeaker. (b) SEM image of the CNT thin film showing that the CNTs are aligned in the drawing direction. (c) A4 paper size CNT thin film loudspeaker. (d) The cylindrical cage shape CNT thin film loudspeaker can emit sounds to all directions, diameter 9 cm, height 8.5 cm.

Fig. Carbon nanotube thin film loudspeakers