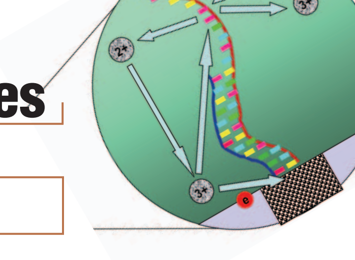

Novel One-Dimensional Nanostructures

by M. Meyyappan, Satyajit Shukla, and Sudipta Seal

Of all the nanoscale materials, carbon nanotubes (CNTs) have received the most attention worldwide.[1] These are configurationally equivalent to a two-dimensional graphene sheet rolled into a tubular structure. With only one wall in the cylinder, the structure is called a single-walled carbon nanotube (SWCNT). The structure that looks like a concentric set of cylinders with a constant interlayer separation of 0.34 Å is called a multiwalled carbon nanotube (MWCNT).

The CNT structure is characterized by a chiral vector (m, n). When m-n/3 is an integer, the resulting structure is metallic; otherwise, it is a semiconductor. This is a unique electronic property that has excited the physics and device community leading to numerous possibilities in nanoelectronics. CNTs also exhibit extraordinary mechanical properties. The Young's modulus is over 1 TPa and the tensile strength is about 200 GPa. The thermal conductivity can be as high as 3000 W/m K. With an ideal aspect ratio, small tip radius of curvature, and good emission properties, CNTs also have proved to be excellent candidates for field emission applications. CNTs can be chemically functionalized, *i.e.*, it is possible to attach a variety of atomic and molecular groups to their ends or sidewalls.

When CNTs were discovered in the early 1990s, arc synthesis and laser ablation were the two most widely used synthesis techniques. More recently, chemical vapor deposition (CVD) has become popular for patterned growth to make devices.[1] Typically, a hydrocarbon feedstock such as methane or acetylene is used in a hot wall reactor which is primarily a quartz tube inserted inside a furnace. A transition metal catalyst such as nickel, iron, or cobalt is applied on the substrate either by sputtering or via a solution containing these metals to be reduced and dried. The growth temperature is in the range of 500-900°C with the upper range corresponding to SWCNT growth. Figure 1 shows a transmission electron microscope (TEM) image of SWCNTs which tend to bundle up like ropes and a scanning electron microscope (SEM) image of MWCNT towers. Each tower consists of billions of nanotubes supporting each other by van der Waals force resulting in a vertical structure; but each nanotube within the tower itself is not really vertical but more like a growing vine.

Plasma enhanced CVD has also become a popular approach recently for growing CNTs.[1] The electric field within the sheath seems to have an effect on growth and it is possible to obtain individual, freestanding, vertically aligned CNTs as shown in Fig. 1c. These multiwalled structures with diameters in the range of 20-100 nm have the inner tubes arranged like stacked cones with an angle of 5-10°; in contrast the angle in an ideal MWCNT is 0°. The structure in Fig. 1c is more appropriately called multiwalled carbon nanofibers or simply carbon nanofibers (CNFs). PECVD also uses hydrocarbon feedstock but it is diluted heavily in H_2, N_2, or argon to avoid production of amorphous carbon. Because nanotube growth is catalyst promoted, the growth temperature is similar to that in thermal CVD. However, with the extensive dissociation of the feedstock in the plasma, the growth precursors may be different in PECVD from thermal CVD for the same feedstock and this may allow for growth at lower temperatures. However, growth possibilities at substantially reduced temperatures are not well established and, in a few reported cases, the resulting structures are of extremely poor quality.

In the following paragraphs, applications of carbon nanotubes[1] which may be of interest to the ECS community, are discussed in an approximate order of expected commercialization potential with the earliest market first. As the feature size of silicon complementary metal-oxide-semiconductor (CMOS) chips continues to decrease with increasing chip density, power dissipation is expected to be a major issue in the coming generations. Power densities of the order of 500-800 W/cm^2 cannot be ruled out, which places a premium on cooling techniques. The thermal conductivity of CNTs is large enough to make them attractive for chip cooling applications. However, the large value is only in the axial direction of the nanotube. As Fig. 1a indicates, the spaghetti-like growth is not ideal for cooling applications and the vertical nanostructures in Fig. 1c are preferable. Note that the disordered nature of the PECVD-grown material results in a lower K value than that of SWCNTs. Recently Ngo *et al.*[2] showed that intercalating the CNFs with a metal like copper produces a composite structure that may meet the heat flux requirements. Early results show a thermal resistance as low as 0.25 cm^2 K/W at 60 psi for this structure.

Intensive research on CNT-based chemical and biosensors is underway across the world. A SWCNT has all its atoms on the surface exposed to the ambient and any slight changes in the ambient environment may modify one or more of the properties of the material. For example, if there is charge transfer between the ambient molecules and CNTs, the conductivity of the nanotubes will change, and monitoring this change may be an effective

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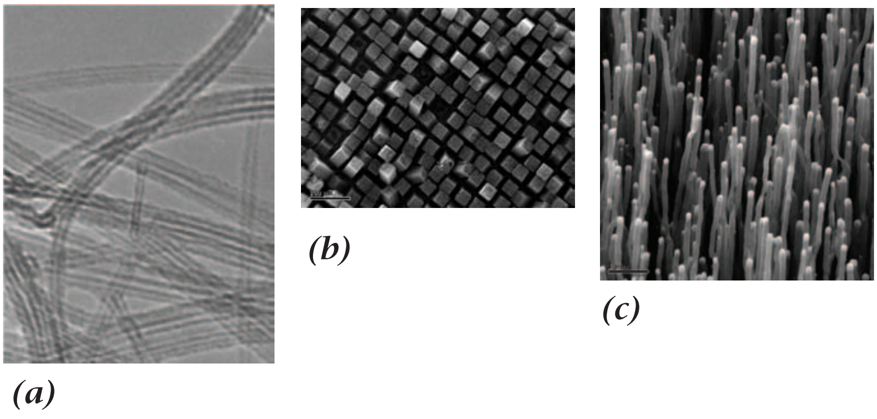

FIG. 1. (a) TEM image of a rope of SWCNTs, (b) towers of multiwalled nanotubes, and (c) PECVD grown carbon nanofibers.

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chemical sensing approach. Taking advantage of this, a chemical field effect transistor (CHEMFET) was fabricated with a SWCNT as a conducting channel.[3] This device is fashioned after thin film transistor sensors using tin oxide as the conducting material. The CNT CHEMFET has been shown to yield reproducible conductivity changes when exposed to gases such as NO_2 and NH_3. A much simpler interdigitated diode structure (see Fig. 2) has also been proposed for chemical sensing applications where a statistically meaningful number of SWCNTs is deposited like a thin film.[4] This approach simplifies the sensor fabrication and has been shown to yield reproducible results for NO_2, NH_3, acetone, benzene, nitrotoulene, etc. While it is expected that charge transfer will be the key mechanism for sensing small molecules like NO_2, this mechanism is unlikely with larger molecules such as nitrotoulene. Such large molecules possibly may bridge two neighboring nanotubes instead in the bundle, thus providing a conducting path. In all these cases, the sensitivity to date has been a few parts per billion (ppb). It is entirely likely that any number of species can produce similar response curves with the CNT chemical sensors. The selectivity is ensured either by doping (for example, Pd for methane sensing) or coating with polymers that are selective to certain species. But the most common approach is to use many sensors (since each of them is very small) in a multiplexing mode and apply pattern-recognition (chemometric) data analysis.

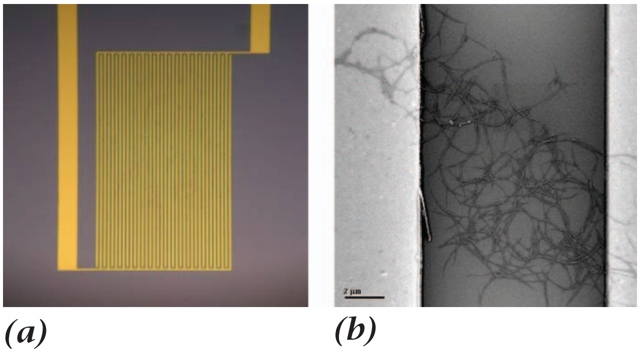

FIG. 2. *(a) A simple interdigitated electrode diode structure for chemical sensing. (b) The nanotubes shown bridge across the structure.*

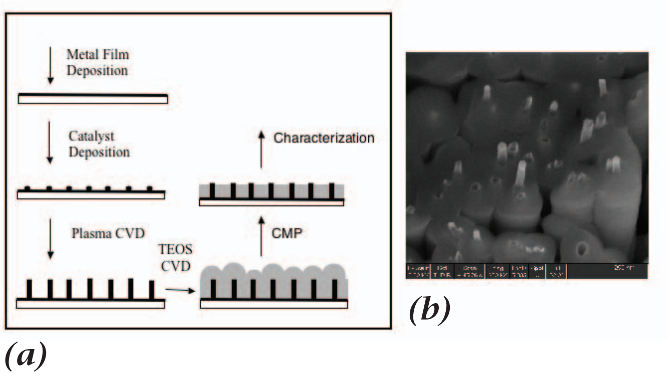

FIG. 3. *(a) Schematic diagram of a CNT nanoelectrode fabrication sequence. (b) Tips of nanotubes sticking out of the surface for functionalization with probe molecules. (TEOS is tetraethyl orthosilicate)*

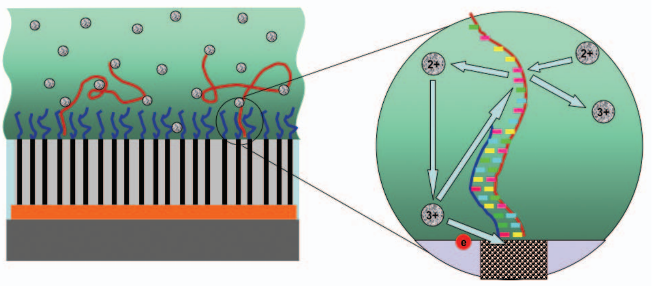

FIG. 4. *Schematic diagram of the carbon nanotube DNA sensor. $Ru(bpy)_3^{2+}$ is used as a metal ion mediator.*

CNTs have been used to develop biosensors as well. Here, the nanotubes are functionalized with a probe molecule (specifically, the CNT tip) for a given target species. The role of the CNT is that of a nanoelectrode and with such a small electrode approaching the size of the analyte molecules, the signal-to-noise problem is significantly reduced. Also, having many CNTs in an electrode array helps to increase the signal. Li *et al.*[5] successfully demonstrated a CNT nanoelectrode fabrication approach for developing biosensors. Figure 3 shows a processing scheme to fabricate the nanoelectrode array which starts with the deposition of a metal underlayer such as Ti, W, or Ta on a silicon wafer. Next, catalyst metal can be sputtered onto the wafer using desirable patterns followed by PECVD of CNFs. In actual applications with the possibility of CNTs encountering fluids, it is important to avoid the nanotubes either collapsing or bunching together. It is also necessary to electrically isolate each nanoelectrode in the array. Both these objectives are met by depositing SiO_2 insulator in the space between the CNFs using thermal CVD. This is followed by a chemical mechanical polishing (CMP) step that yields a surface of SiO_2 with nanotube tips sticking out (see Fig. 3). Now deoxyribonucleic acid (DNA) strands or other probe molecules can be attached to these tips. Li *et al.*[5] demonstrated such DNA functionalization of the tips and subsequent hybridization with complementary strands. They used $Ru(bpy)_3^{2+}$ as a mediator for chemical amplification as shown in the schematic diagram in Fig. 4 and demonstrated a detection sensitivity of well below 1000 DNA molecules. This approach finally has overcome the limitation of electrochemical detection based on microelectrodes in terms of a lower sensitivity relative to conventional laser-based fluorescence techniques. The use of nanotube nanoelectrode arrays in Ref. 5 not only provides sensitivity approaching the fluorescence technique, but is also label-free because the inherent guanine bases in the DNA target serve as signal-generating moieties. The CNT nanoelectrode approach is amenable for direct integration with microelectronics and microfluidics for developing fully automated multiplexed chips for rapid

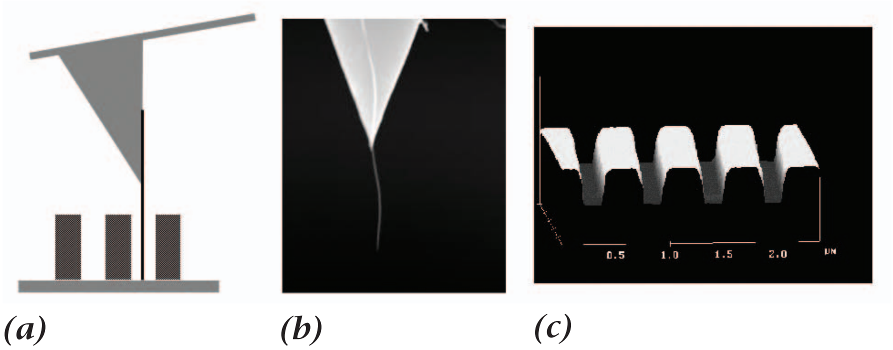

Fig. 5. CNTs as AFM probes. (a) Schematic diagram, (b) TEM image of a MWCNT probe, and (c) image of a deep UV pattern generated by interferometric lithography.

molecular analysis in applications such as pathogen detection, cancer diagnosis, and other lab-on-a-chip needs.

Atomic force microscopy (AFM) has become a powerful technique for imaging metallic, semiconductor, or dielectric thin films as well as biological materials. In semiconductor manufacturing, AFM is also finding its way as a critical dimension metrology tool. The conventional micromachined silicon or Si_3N_4 tips are typically 20-30 nm at the end and provide reasonable image resolution. However, their wear rate is high and they also can break any time during imaging. SWCNT tips with 1-2 nm diameters have been shown to provide not only extraordinary nanoscale resolution but also to be highly wear-resistant.[6] MWCNT probes have been used to perform profilometry of via holes and trenches as well as lithographic patterns as shown in Fig. 5. The nanotubes may be grown directly by CVD at the end of an AFM cantilever; but this approach produces only one probe at a time. Plasma CVD technique may be used to grow the CNT probes at desired angles on a wafer for large scale production of CNT probes for AFM.

CNTs have the potential to be the next-generation interconnect material for local and global wiring applications. Their current carrying capacity is extremely high; even at current densities of 10^9 A/cm^2 and at elevated temperatures, carbon nanotubes do not appear to have any problems whereas copper begins to suffer from electromigration at densities exceeding 10^6 A/cm^2. In addition, CNTs are mechanically robust hollow cylinders of desirable aspect ratio. While such advantages are obvious, a clear processing strategy to integrate nanotubes as interconnects in silicon CMOS fabrication is needed urgently.[7] The fabrication sequence in Fig. 3 for biosensors is also a viable approach to produce CNT interconnects for dynamic random access memory (DRAM) applications with a metal deposition step following CMP. Instead of the traditional etching (of SiO_2) – deposition (of copper interconnect) – CMP sequence, this approach involves deposition (of CNT interconnects) – deposition (of dielectric) – CMP routine, thus eliminating etching altogether. The height and aspect ratio of the via and interconnect are controlled by PECVD. Ngo *et al.*[8] have demonstrated an individual via resistance of about 18 Ω whereas the ultimate goal is about 1 Ω.

Field emission devices (FEDs) have been of interest in many applications including displays, lighting elements, electron source for instruments such as SEM, and microwave source. Traditionally, Si, Mo, and W have been used to produce field emission displays (FEDs) but recently CNTs have been shown to require an order of magnitude less field strength to create comparable emission. For example, a threshold current of 10 mA/cm^2 can be produced with an electric field of 1-3 V/µm in CNTs compared to 50-100 V/µm in silicon. In addition, the small tip radius of curvature and the large aspect ratio of CNTs are also highly desirable attributes for field emission. Prototype 40 in. color displays using CNT FEDs have been demonstrated in Japan and Korea. The National Aeronautical and Space Administration (NASA) has scheduled to fly an X-ray fluorescence and diffraction instrument to Mars in 2009 with the X-ray tube based on CNT field emission. The miniaturized X-ray tube allows an order of magnitude reduction in the size of the instrument and a considerable reduction in its power consumption.

Finally, diodes, transistors, and circuit elements using CNTs as the conducting channel for logic and memory applications have been demonstrated.[1] While these early demonstrations are impressive, commercial devices are a decade or more away if at all technically feasible and economically viable. Current challenges include lack of selectivity of semiconductor *vs.* metallic nanotubes desirable for device fabrication. Even if this can be solved in the foreseeable future, it does not make much technical or economical sense to push CNT as a conducting channel in an otherwise CMOS architecture and fabrication scheme. As feature scale reduction in Si CMOS continues, challenges involving heat dissipation, lithography, dielectrics, etc. are commanding enormous attention and investments currently. The use of CNTs does not inherently solve or make any of these problems go away. In the absence of an order of magnitude improvement over silicon in performance for any given future generation device or a demonstration of circumventing some key bottleneck (such as gate leakage, lithography need), the industry will not embrace any new technology. In this regard, the future of CNTs in nanoelectronics is murky at present.

In the remainder of this article, the gas sensing application is considered in detail using nanowires and nanotubes. Semiconductor oxide gas sensors based on the resistance change mechanism are the most popular experimental and commercial gas sensors. Traditionally, thick films and pellets of semiconductor oxides were utilized for the gas sensing application. However, in the last two to three decades due to the rapid growth in the silicon-based industries, utilization of thin films of semiconductor oxides have been potentially realized, because these materials can be synthesized easily with the processes compatible with integrated circuit manufacture. Higher gas sensitivities and lower response times are the additional gains in using semiconductor oxide thin films. Commercially available thin film semiconductor oxide sensors, however, still lack in being able to sense part per million or part per billion level gases with very high sensitivity and minimum response time at lower operating temperatures. Analyte gas selectivity has been another major issue with these types of thin film sensors.

After the invention of carbon nanotubes,[9] the focus has been changing drastically from thin films to other forms of semiconductor oxides, as depicted in Fig. 6, for optimizing the detection time and the gas sensitivity at lower operating temperatures. Along with the nanocrystalline thin films, various forms of semiconductor oxides, such as single nanowire, parallel assembly of nanowires, random network of nanowires, and nanotube arrays have all been recently explored. Some typical gas sensitivity results reported for these quasi-one dimensional forms of semiconductor oxides are summarized in Table I. It appears that

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the maximum gas sensitivity has been obtained at room temperature for the thin film sensors but the response time is as high as a few minutes, which may somewhat limit its practical application if early gas detection is a major criterion. Further scrutiny of Table I reveals that the gas detection time associated with semiconductor oxide sensors can be reduced by changing their form. In this respect, a single or random network of nanowires of semiconductor oxides is the most suitable form for achieving the gas detection time of a few seconds at lower as well as at higher operating temperatures. However, extremely low gas sensitivity of a single or random network of semiconductor nanowires is a significant problem in view of the false leak alarm. Hence, the trade-off between gas sensitivity and response time may be resolved using the proper form of the semiconductor oxides.

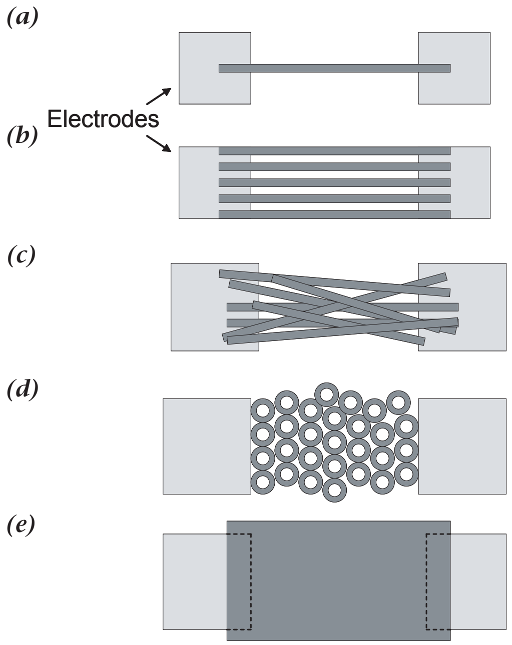

Fig. 6. Schematic diagram describing the different forms of semiconductor oxides investigated in the literature for the gas sensing application.

Recently, SWCNTs and MWCNTs have been synthesized and utilized for the gas sensing application. Some typical gas sensing results reported in the literature, except the work described earlier, for these new gas sensing materials are tabulated in Table II and can be compared with the gas sensing properties of semiconductor oxide gas sensors in Table I. Three different forms of carbon nanotubes, viz. single, parallel aligned, and random network have been investigated for gas sensing. Comparison of the data in Tables I and II surprisingly reveals that, relative to the semiconductor oxide gas sensors, carbon nanotubes exhibit very low gas sensitivity (<2) and high detection time (5-2700 s). Moreover, the recovery time associated with the CNT-based gas sensor is a few hours.[22] Due to their poor gas sensitivity properties as reported in the table, the use of carbon nanotubes in CHEMFETs and other approaches as a gas sensing material does not provide any added advantage over the use of the nanowires of semiconductor oxides. In this regard, the interdigitated electrode array (IDA) approach discussed earlier has demonstrated part per billion level sensing for various gases and vapors and is currently being explored for manufacturing. ■

Summary

Carbon nanotubes and other one-dimensional (1-D) nanostructures are novel materials suitable for a range of industrial applications including chip cooling, FEDs, chemical and biosensors, AFM tips, interconnects, and conducting channels. Extensive research, however, is still needed to exploit this new class of materials and translate them from a laboratory curiosity to the commercial scale.

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Table I. Typical gas sensing results reported recently for the varous forms of semiconductor oxides.

Sensor material	Sensor form	Synthesis method	Operating temperature $(^{0}\mathrm{C})$	Gas (amount)	Sensitivity (R_{air}/R_{gas})	Response time(s)	Ref.
SnO_2	Single nanobelt	Vapor phase evaporation	200	C_2H_5OH (250 ppm) NO_2 (0.5 ppm)	2.0 30.0	Few seconds	10
SnO_2/Pd	Single nanowire	Thermal evaporation	200	H_2 (?)	2.5	2.5	11
Pd	Single nanowires	Electrochemical deposition	25	H_2 (5%)	3.5	75.0 (ms)	12
In_2O_3	Random network of nanowires	Carbothermal reduction	370	C_2H_5OH (1000 ppm)	30.0	10.0	13
ZnO	Random network of nanowires	Thermal evaporation	300	C_2H_5OH (200 ppm)	50.0	15.0	14
TiO_2	Nanotubes array	Anodization	290	H_2 (1000 ppm)	10000.0	200.0	15

Table II. Typical gas sensing results reported recently for the various forms of CNTs.

Sensor material	Sensor form	Synthesis method	Operating temperature (^{0}C)	Gas (amount)	Sensitivity (R_{air}/R_{gas})	Response time(s)	Ref.
SWCNT-Pd	Single tube	Patterned CVD growth	Ambient	H_2 (400 ppm)	2.00	5-10	17
SWCNT	Parallel aligned	PECVD	165	NO_2 (100 ppb)	1.28	2700	18
SWCNT-PABS	Random network	Arc discharge	32	NH_3 (100 ppm)	0.25	60	19
SWCNT-Pd	Random network	Arc discharge	25 250	H_2 (0.5-2.0%)	1.10 1.12	120	20
MWCNT	Random network	Modified PECVD	25	NH_3 (200 ppm)	0.70	180	21
CNT	Random network	PECVD	165	NO_2 (100 ppb)	0.56	Few minutes	22

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