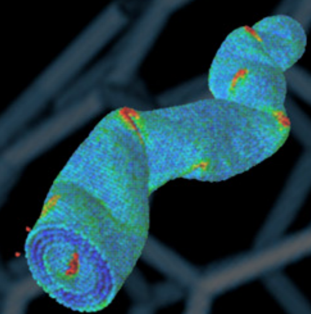
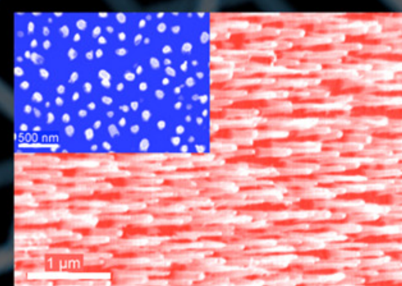
Nano and Bio Technology Research at NASA Ames

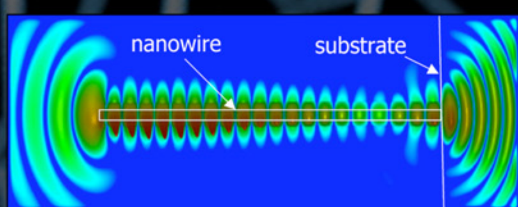
M. Meyyappan and Harry Partridge
NASA Ames Research Center
Moffett Field, CA 94035



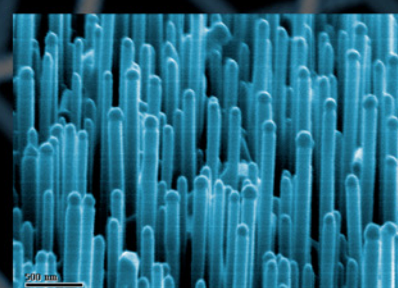
Nano-Mechanics/Materials



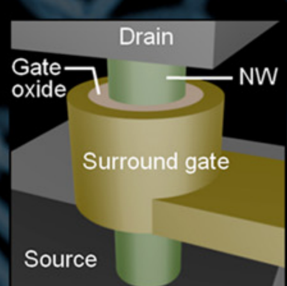
CNTs by PECVD



Nanowire Lasing



ZnO Nanowires



Vertical, Surround-gate Transistor

CNT Emitter

Revised: February 1, 2006

Nano and BioTechnology Research at NASA Ames

M. Meyyappan and Harry Partridge
NASA Ames Research Center
Moffett Field, CA 94035

Abstract

This article provides an overview of nanotechnology and biotechnology research at NASA Ames Research Center and covers current results in the areas of carbon nanotube (CNT) growth and characterization and functionalization, nanotubes in scanning probe microscopy, inorganic nanowires, biosensors, chemical sensors, nanoelectronics optoelectronics, computational nanotechnology, quantum device simulation, and computational optoelectronics.

Introduction

Advanced miniaturization is a key thrust area to enable new science and exploration missions for which ultrasmall sensors, power sources, communication, navigation, and propulsion systems with very low mass, volume and power consumption are needed. Revolutions in electronics and computing will allow reconfigurable, autonomous, "thinking" spacecraft. Nanotechnology presents a whole new spectrum of opportunities to build device components and systems for entirely new, bold space architectures such as networks of ultrasmall probes on planetary surfaces, micro-rovers that drive, hop, fly and burrow, and collection of microspacecraft making a variety of measurements.

NASA Ames started an Integrated Product Team (IPT) on Devices and Nanotechnology in FY 97 to conduct basic research in the emerging field of nanotechnology as well as in semiconductor device physics, computational electronics and optoelectronics, and computational chemistry in materials processing. This effort was renamed as NASA Ames Center for Nanotechnology (NACNT) couple of years later. The research focus, summarized in Table 1, covers a wide range of subjects: carbon nanotube and inorganic nanowire (CNT) synthesis, characterization, functionalization, nanoelectrode fabrication for sensor development, chemical and biosensor development, nanoelectronics, nano-optoelectronics including detectors and lasers, thermoelectric devices, application of CNT in atomic force microscopy (AFM), thermal, radiation and impact protection shields using nanomaterials, development of quantum device simulator, computational optoelectronics and computational nanotechnology. This article provides selected results in the above areas. A complete current publication list and reprints from the Ames group as well as descriptive project summaries can be found in the NACNT website http://www.ipt.arc.nasa.gov. This website also features a nanotechnology gallery containing videos and images [1].

Table 1.

Research Focus	
* **Carbon Nanotubes** • Growth (CVD, PECVD) • Characterization • Chemical functionalization • AFM tips - Metrology - Imaging of Mars Analog - Imaging Bio samples • Electrode development • Biosensor • Chemical sensor • Interconnects • Thermal Interface Material • Gas Adsorption • Device Fabrication * **Inorganic Nanowires** • Growth (VLS, Sol-gel) • Characterization • Nanoelectronic devices • Detectors, lasers • Thermoelectric devices	* **Nanoelectronics** • Synthesis of organic molecules • Characterization • Device fabrication * **Nanomaterials** • Thermal, Radiation, Impact protection * **Computational Nanotechnology** • CNT - Mechanical, thermal properties • CNT - Electronic properties • CNT based devices: physics, design • CNT based composites • CNT based sensors • DNA transport • Nanowires: transport, thermoelectric effect • Transport: molecular electronics * **Quantum Computing** * **Computational Quantum Electronics** • Noneq. Green's Function based Device Simulator * **Computational Optoelectronics**

Carbon Nanotubes

Growth and Characterization

In the early days of nanotechnology research, CNTs were primarily grown by laser ablation and carbon arc techniques by various research groups across the world. Both approaches produce single wall CNT in small quantities scraped off the cooler walls of the reactor. In the last few years, chemical vapor deposition has emerged as an alternative approach. CVD, a workhorse in silicon microelectronics, is ideally suited to grow nanotubes on patterned substrates if one is interested in investigating nanoelectronic devices or sensors. Ames operates two CVD reactors to grow nanotubes on substrates. The feed gas may be CO or some hydrocarbon gas, and typical growth temperatures for multiwall carbon nanotubes is 500-800° and 900° for single-walled nanotubes.

The CNT growth is catalyzed by transition metals such as nickel, iron or cobalt. The catalyst mixture can be applied to the substrate by solution chemistry followed by calcinations and few other steps. Parameters controlling growth appear to be numerous: nature of feedgas and composition, flow rate, temperature, type of catalyst, catalyst preparation technique, and substrate material. To date, no research group has been able to precisely control CNT diameter or chirality. Since the number of variables involved is very large, a combinatorial chemistry approach has been used, as pioneered by Alan Cassell at Ames, for catalyst optimization in CNT synthesis [2]. Figure 1 shows a bundle of multiwall CNTs grown by this approach. Figure 2 shows a multilayer assembly of multiwall carbon nanotubes grown using CVD approach. The densities of the upper and lower layers are different and a controlled assembly would be useful in the preparation of separation membranes and composites [3].

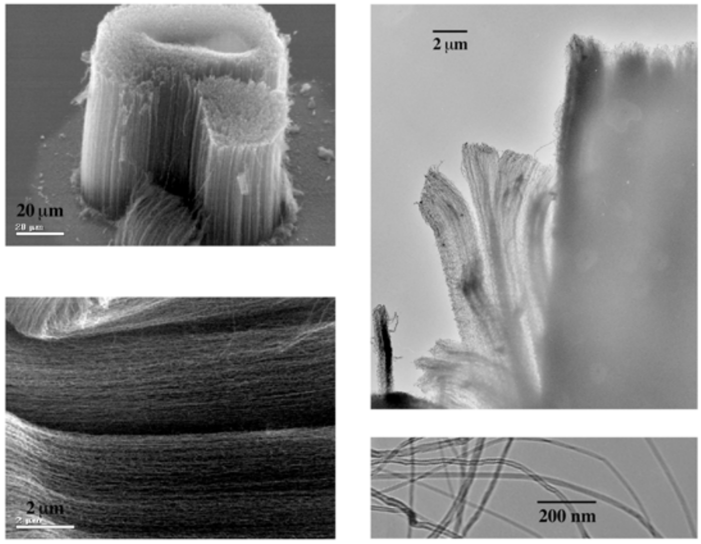


Fig. 1. Multiwall carbon nanotubes grown by CVD

We have also investigated catalyst preparation through direct ion beam sputtering which allows easy confinement of the catalyst within small patterns. It was found that adding an underlayer of Al allows increased nucleation of the nanoparticles needed for CNT growth; this metallic layer also allows tuning of the conductivity of the substrate [4, 5].

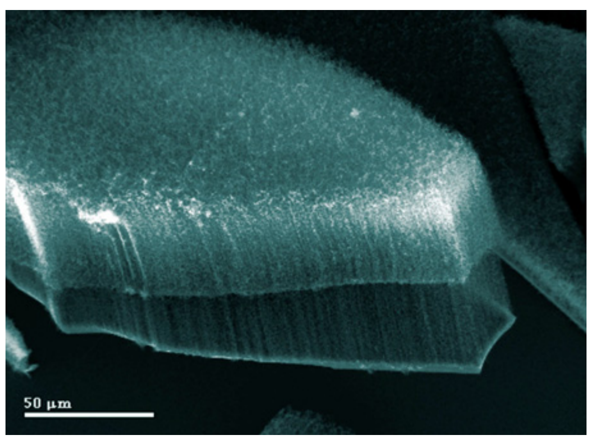


Fig. 2. Multilayer assembly of nanotubes

Figure 3 shows single wall carbon nanotubes prepared by CVD on a patterned grid using the above approach [4]. Both thermal CVD [4, 5, 6] and plasma CVD [7-10] are routinely used at Ames to grow SWNTs and MWNTs. Thermal CVD has allowed SWNT and MWNT growth on patterned substrates. In the case of MWNTs, continued growth over 10 minutes yields nice towers of MWNTs. These towers consist of millions of MWNTs supporting each other by van der Waals force; individual nanotubes, in high magnification, appear to grow like vines. In contrast, it is possible to obtain individual, free-standing, vertically-aligned structures with plasma CVD as seen in Fig. 4 [7-9]. But it is important to recognize that these structures are not MWNTs according to conventional definition, where each wall should be perfectly parallel to the central axis.

The nanostructures in Fig. 4 have interior walls exhibiting a small angle with respect to the central axis. This stacked-cone shape material is preferably called multiwalled carbon nanofibers (MWNFs) to distinguish them from MWNTs [7]. These are also known as vertically aligned carbon nanofibers (VACNFs). The plasma reactor commonly used at Ames to grow these MWNTs and MWNFs is a dc glow discharge reactor; in addition, an inductively coupled reactor with an independent rf bias at the bottom electrode holding the substrate is also used [10].

The nanotube characterization at Ames is done using scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and UV-Vis spectroscopy.

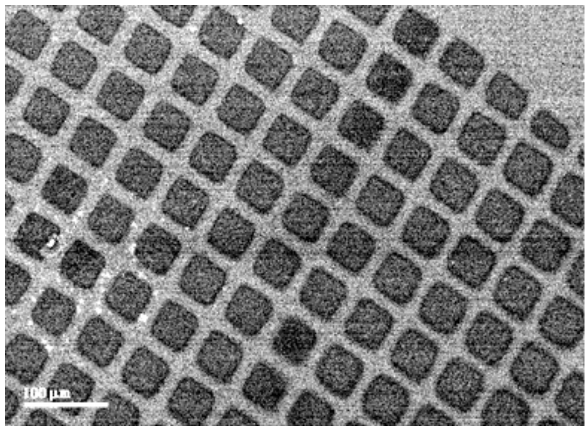


Fig. 3. Single Wall Carbon Nanotubes by CVD

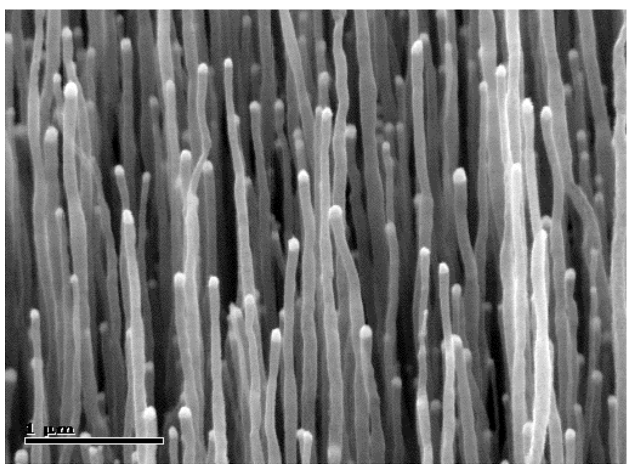


Fig. 4. Plasma CVD of MWNFs

<u>Functionalization of Nanotubes</u>

Various applications call for the need to attach chemical functional groups to the sidewall of CNTs. For example, it is believed that chemical functionalization may provide the “velcro effect” needed for incorporating CNTs in a host matrix for developing composites. Attaching fluorine along to the sidewall makes CNTs nearly insulating, changing the conductivity orders of magnitude. Regardless of the application, a common approach to functionalizationn is wet chemistry. While a wet chemistry approach is simple, it is not scalable, deals with large quantities of chemicals which need to be discarded and suffers from poor efficiency and a host of other issues which were faced by the semiconductor community 20 years ago when dealing with wet chemistry for etching semiconductors, oxides and metals. The innovation then was the cold plasma based chemistry for etching. Cold plasmas or glow discharges can be used for functionalization of CNTs as well. Khare and coworkers [11-14] demonstrated this approach by using a simple microwave cavity to generate a plasma that contains the required species for functionalizations. They have demonstrated functionalization of CNTs with atomic hydrogen using a H_2 plasma, atomic fluorine with a CF_4 plasma and atomic nitrogen with N_2 or NH_3 plasma. In all cases, a very small quantity of source gas is all what is required. Functionalization also appears to be rapid. Evidence of attaching the chemical groups was obtained from appropriate FTIR, Raman and UV signals.

Nanoelectrode Fabrication

The MWNFs are ideal for developing nanoscale electrodes. They range in 20-100 nm diameter. Their density and hence, the average spacing between individual MWNFs can be varied by varying the thickness of the catalyst films. Of course, if one wishes a precise control on the spacing, then catalyst patterning by e-beam lithography would be ideal. In applications as electrodes, particularly with electrochemical approaches involving electrolytes and indicators, it is important to maintain the rigidity of the nanostructures. For this reason, gap-filling techniques were developed to fill the spacing between MWNFs with a dielectric such as SiO_2 or spin-on-glass. TEOS CVD was used to deposit SiO_2 followed by chemical mechanical polishing to planarize the top surface (see Fig. 5). Now, only the very tip of the MWNFs are exposed while the rest are buried inside the SiO_2. Electrical characterization of these tips indicate that they function as electrodes as desired [15] and hence, are suitable for attaching DNA or other chemical groups. These nanoelectrode arrays are useful for biosensor development as described below.

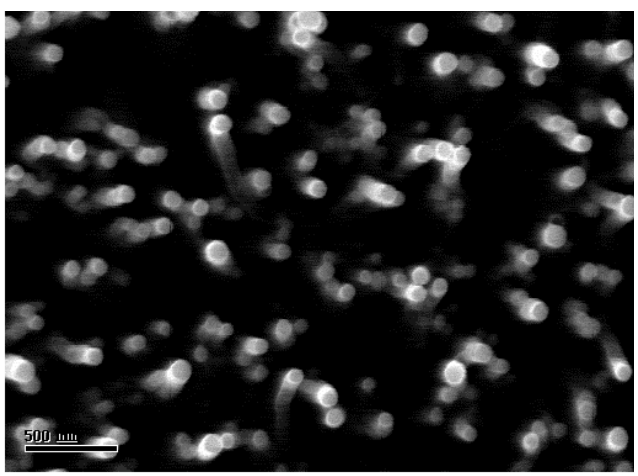


Fig. 5. SEM image of MWNFs after encapsulated in SiO_2

Biosensor for Various Applications

Jun Li and coworkers at Ames prepared the above electrode ensemble and attached DNA to the MWNF tips. The attachment is due to covalent bonding and they have also demonstrated hybridization by bringing in a complementary strand for the probe DNA molecule. In addition to the evidence from fluorescence microscopy for these events, they have also used an electrochemical indicator and obtained signals that are proportional to the amount of guanine in the target sequence [15-18].

A major area of focus in CNT applications at Ames is development of biosensors for various applications using the above demonstration. To date, a 30 sensor die on a 4" wafer has been fabricated. The application focus ranges from water quality and bacteria monitoring (for NASA's crew exploration vehicle and other human habitats) to biothreat monitoring for homeland security and cancer diagnostics. The latter work, conducted through funding from National Cancer Institute, involves development of a prototype biosensor catheter that permits detection of specific oligonucleotide sequences that serve as molecular signatures of cancer cells. A critical element of this technology involves the ability to functionalize the tip of a nanotube array with (a monolayer of) probe molecules as described in the previous paragraph.

The nanoelectrode array is also being used for deep brain stimulation (DBS) to treat disorders such as Parkinson's disease and epilepsy. This NIH funded work focuses on developing a 3-d interface between the neural tissues and solid state electronics using the nanoelectrode array [19].

Chemical Sensors

There is a tremendous need for chemical sensors with high sensitivity in the parts per million (ppm) to parts per billion (ppb) level. NASA's needs included sensors for cosmochemistry (identification of atmospheric constituents of various planets), earth observation (greenhouse gases), and leak detection in the shuttle and future crew exploration vehicle (CEV) that involves sensing of hydrazine and N_2O_4. Chemical sensors are sorely needed for the detection of toxic industrial chemicals and nerve agents for homeland security applications. NACNT is developing SWNT based sensors for the above purpose.

Nanomaterials in general have a very large surface area and we have characterized that SWNTs possess a surface area of about 1600 m^2/g [20]. This large surface area translates into large adsorption rate of gases and vapors. This adsorption can lead to a change in some specific properties of the SWNTs, for example, conductance, capacitance etc. Indeed SWNT field effect transistors have been fabricated wherein a single SWNT or a film of multiple SWNTs forms the conducting channel. The conductivity of this device has been shown to change reproducibly upon adsorption of gases like NH_3 and NO_2, which forms the basis for chemical sensing. However, three terminal transistors are expensive and complex to fabricate and therefore, Jing Li and coworkers at NACNT came up with an innovative alternative involving an interdigitated electrode shown in Fig. 6. This device is fabricated using single microfabrication steps and purified SWNTs are solution-cast across the electrode to form the conducting channel.

Figure 7 shows the sensor signal for repeated doses of NO_2 wherein the response is fairly rapid. The projected sensitivity is about ~40 ppb. The sensor recovery time (the time to recover to baseline after the source is removed) needs further improvement; shining a UV source accelerates the desorption of the vapor from the nanotubes thus accelerating sensor recovery. This is an area that is currently being investigated for further improvement. To date, the sensor has been tested for NO_2, NH_3, CH_4, Cl_2, HCl, toluene, benzene, acetone, formaldehyde and nitrotoulene [21-23].

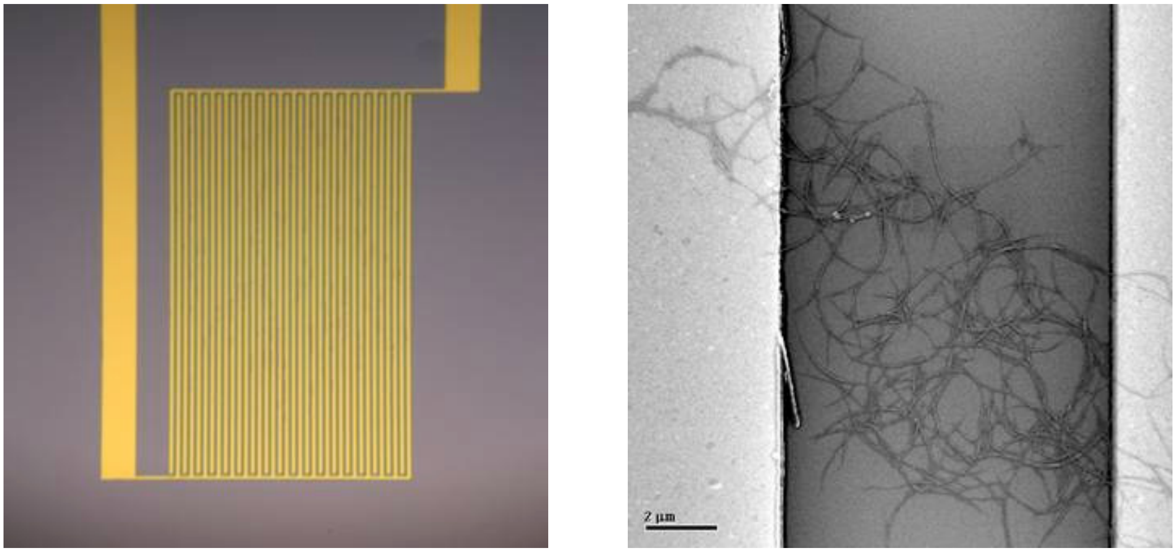


Fig. 6. Interdigitated electrode structure for chemical sensors.

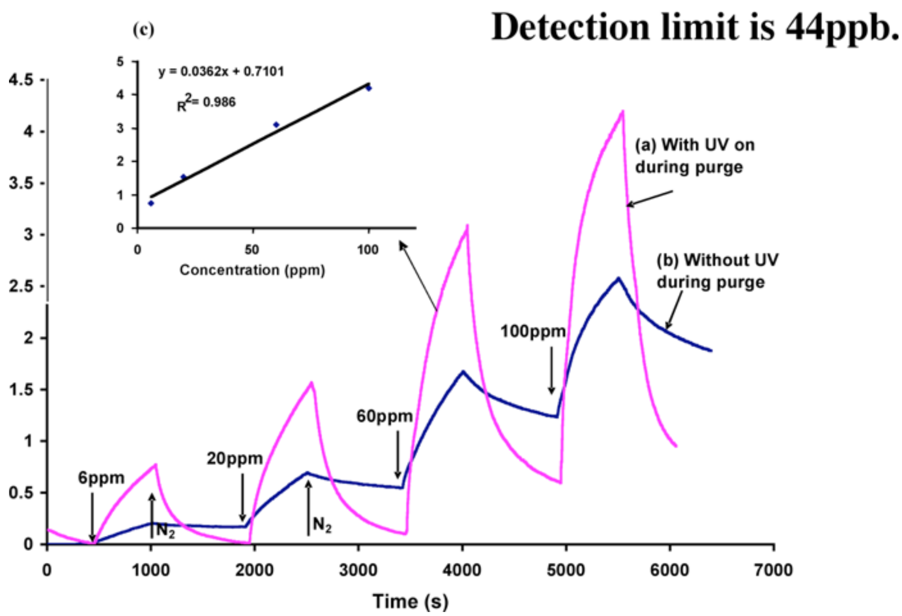


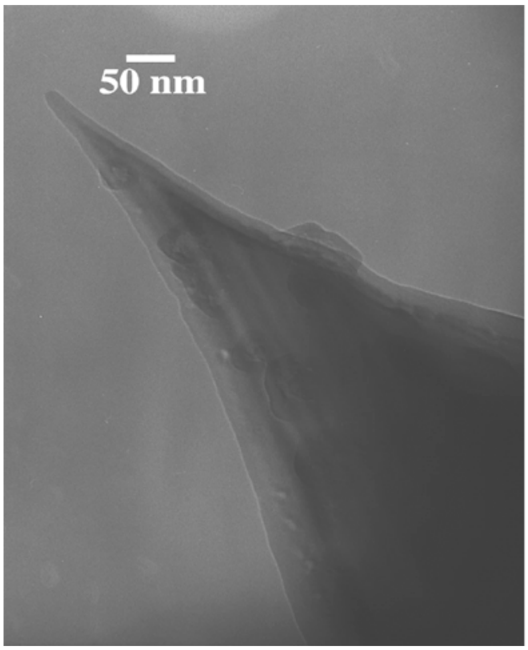
Fig. 7. Sensor response to NO_2

<u>Nanotubes in Catalysis</u>

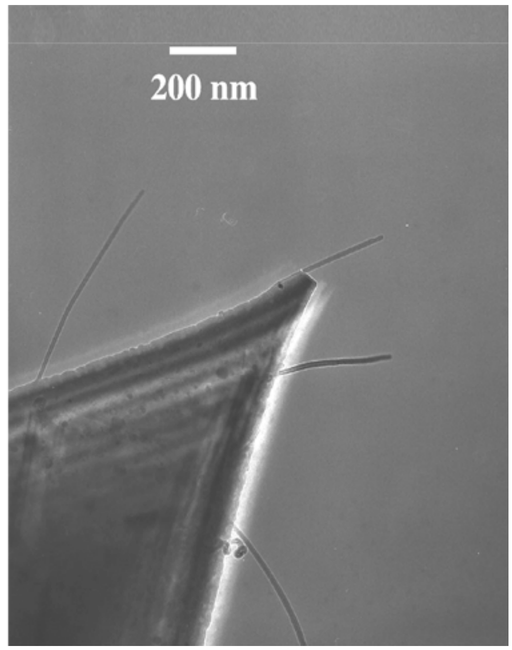
CNTs have been postulated to have a high surface area which would be useful in catalysis, gas adsorption and related applications. Though theoretical estimates put the surface area in the 3000 m^2/g range, experimental results have been well under 1000 m^2/g. Jing Li and coworkers demonstrated a surface area of 1580 m^2/g for purified HiPCo SWNTs [20]. They used a two step purification process with the first step involving a debundling procedure followed by a step to clean up the metal impurities and the small amount of unwanted amorphous carbon. The large surface area based on N_2-adsorption isotherm studies have led them to investigate both physisorption and chemisorption aspects of adsorbing CH_4, NO_2, NO, CO_2, etc. onto HiPCo samples. The goal of their study is to investigate the suitability of SWNTs as catalysts or support material for waste remediation in long voyage crew cabins [24].

CNT in Microscopy

CNT is an ideal tip for use in AFM [25, 26] since it is robust and can be just a few nanometers in diameter. However, manually attaching a CNT to the tip of a cantilever can be arduous. Our group has been able to use CVD to directly grow single wall nanotubes on the AFM cantilever. Figure 8 shows an example of the effort. We have also developed an electrochemical approach to easily attach a multiwall nanotube to the AFM cantilever [26].



TEM Micrograph of Electro-deposited Catalyst on Tip of AFM Cantilever



TEM Micrograph of Shortened NT Synthesized by CVD

Fig. 8. Nanotube probe directly grown on AFM cantilever.

The AFM with nanotube tip is currently used to image and study simulated Mars dust. Figure 9 shows an image of Red Dune Sand (from Western Australia) which is a Mars analog. The CNT tip - only a few nanometers in diameter - is able to offer extraordinary resolution in imaging the dust particles. In addition, the robustness of CNT provides long lasting tips in contrast to the quick wearing of silicon tips. Our other accomplishments with CNT probes include metrology applications (for example, a profilometer) and nanoscale imaging of semiconductor surfaces. Figure 10 shows an AFM image of a thin iridium film obtained using a single-walled nanotube tip. The resolution here is much better than conventional silicon tips [25]. These CNT probes have also been used to image biological samples both in the dry form and in their native aqueous environment [27]. The latter is accomplished by coating the nanotube probe with ethylene diamine to render the probe hydrophilic in order to be able to image liquid samples.

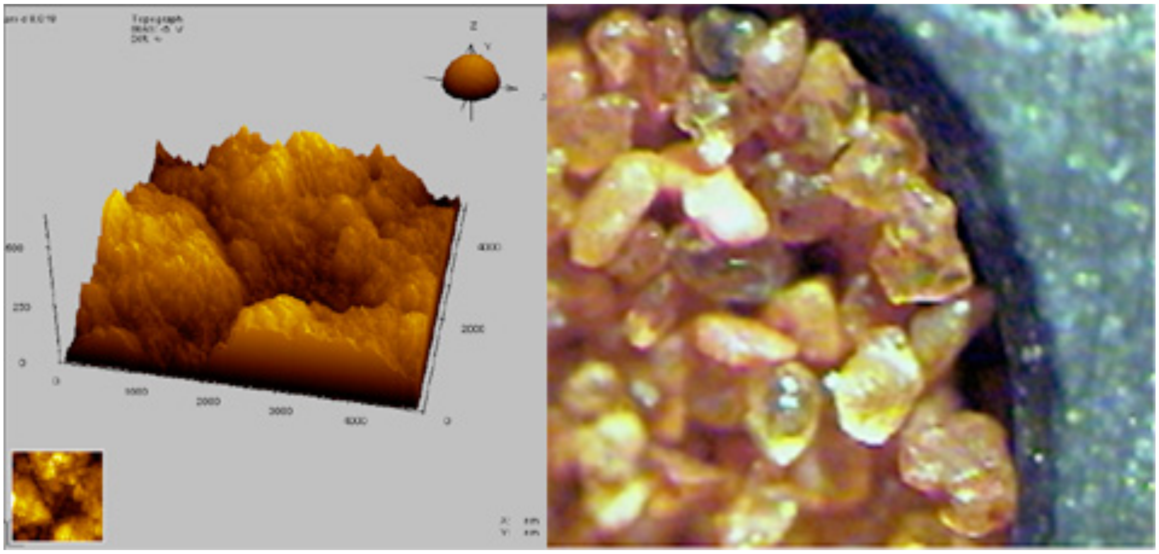


Fig. 9. AFM Image of Red Dune Sand (Mars Analog) obtained using a nanotube tip (left) compared to an image using optical microscope (right).

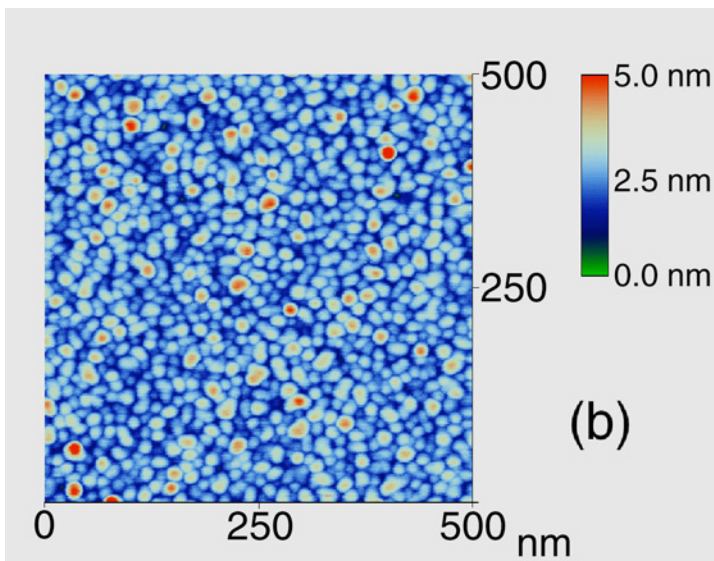


Fig. 10. AFM image of iridium film using a SWNT tip

<u>CNT Field Emission for Instrumentation</u>

Carbon nanotubes are well known for their field emission characteristics as they exhibit large aspect ratio and a small tip radius of curvature in addition to good electron affinity values. While much of the work in the literature focuses on field emission for flat panel displays, NACNT has been working on exploiting this for developing science instruments for planetary exploration. Optimized emission conditions ideal for generating X-rays have helped to develop an X-ray tube shown in Fig. 11 that can power an X-ray diffraction spectrometer [28]. In addition, current work focuses on electron source for miniaturized mass spectrometer and miniaturized SEM.

Fig. 11. CNT based X-ray tube

CNTs as Interconnects and in Thermal Management

Carbon nanotubes exhibit very high electrical and thermal conductivities. Their current carrying capacity is also extremely high, for example up to 10^9 A/cm^2 where copper begins to suffer from electromigration at about 10^6 A/cm^2. Jun Li, Alan Cassell and coworkers have developed a bottom up process [29] to integrate PECVD CNFs as interconnects for DRAM applications. The as-grown CNFs are gap-filled with SiO_2 followed by CMP and ready for top metallization. In a series of publications [29, 30], progressive improvement in the resistance of the interconnects has been reported. A CNF-Cu composite also has been developed as a thermal interface material for chip cooling applications [31]. This technology has been licensed to a Bay Area company specializing in chip cooling solutions.

Inorganic Nanowires

Whereas the carbon nanotube research continues to address the challenge of controlling the chirality (thus creating the ability of producing metallic or semiconducting of nanotubes of specified bandgap at will), quietly a new technology is emerging based on inorganic nanowires. Materials such as Si, GaAs, InP, ZnO and other oxides have long been prepared as very thin films of 1-20 nm which propelled advances in lasers, transmitters, receivers and sensors, taking advantage of the quantum properties of these confined layers. Shrinking this by another dimension from 2-d to 1-d, it is now possible to grow most of these structures as 1-d nanowires. Researchers at Ames have made tremendous progress in growing nanowires of ZnO, SnO_2, InSb, silicon, germanium and others [32-38]. Fig. 12 shows very nicely aligned ZnO nanowires grown on a sapphire substrate. The choice of sapphire substrate is dictated by the minimum mismatch with ZnO. The bandgap of these ZnO nanowires makes them useful in developing blue lasers and blue LEDs.

Though nanowires have been grown by various techniques such as templating and evaporation, our approach involves the vapor-liquid-solid mechanism. Here, a thin catalyst metal is deposited on the growth substrate which melts at the growth temperature and forms tiny beads. The source material, either sublimated from the solid source (such as zinc oxide powder) or reacted with graphite powder in carbothermal reduction (ZnO powder + graphite powder) or generation through chemical reactions (silane + H_2 reaction for silicon wires), dissolves into the tiny droplets and when supersaturation is reached, the material precipitates as nanowires.

The nanowires are characterized using SEM, TEM, Raman spectroscopy, FTIR, photoluminescence and other techniques.

Nanowire Based Electronic Devices

Bin Yu and coworkers have been working on germanium based devices for memory and logic applications. For this they have come up with a nanowire-on-insulator (NOI) concept similar to the well known silicon on insulator (SOI concept). Figure 13 shows a germanium wire bridging two contacts grown on an insulating layer. The I-V characteristics of this device are shown on Fig. 14 which exhibit an ambipolar behavior due to the Schottky contacts. Novel device configuration such as vertical devices with either a top gate or surround-gate have also been demonstrated [39, 40] using wide band gap materials with future work focusing on silicon and germanium nanowires.

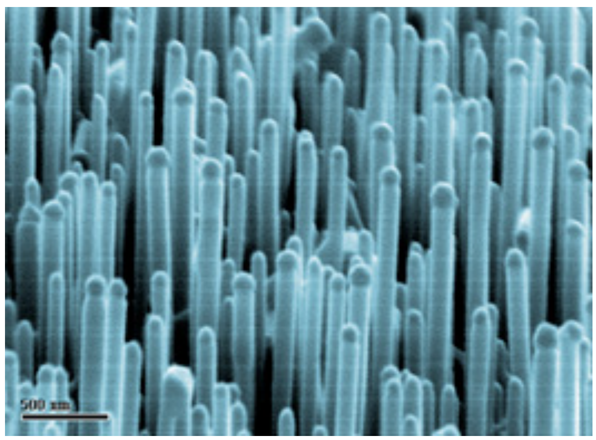


Fig. 12. ZnO Nanowires

While most of the work in the literature focuses on using gold as a catalyst, Bin Yu and colleagues have avoided it since gold is thought to be a contaminant in device processing. They have come up with alternatives of low melting metals such as Ga or In which, not only avoid contamination issue, but also allow growth at much lower temperatures (350° C vs. 800° C).

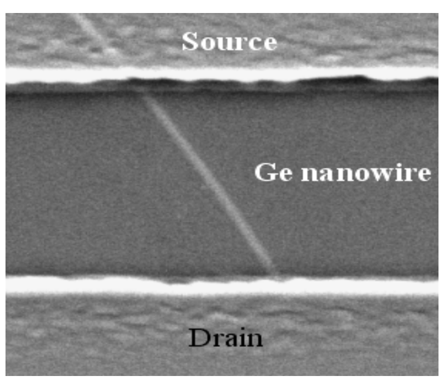


Fig. 13. Germanium nanowire on insulator

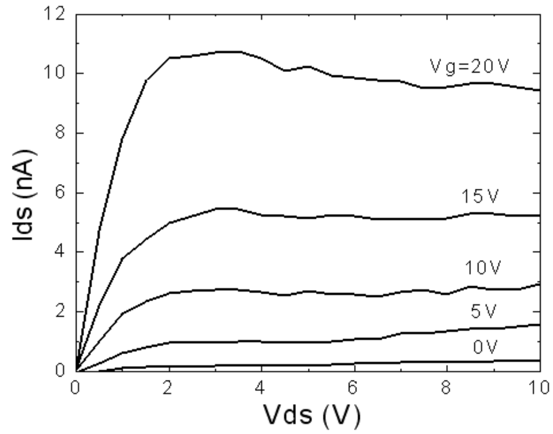


Fig. 14. I-V characteristics of Ge-NOI device

Computational Nanotechnology

Extensive investigations using computational simulations on the electronics, mechanical and other properties of nanotubes have been undertaken by the Ames nanotechnology group. SWNTs exhibit remarkable mechanical properties, for example, a Young's modulus of over 1 TPa and tensile strength of about 200 GPa. They also have been unique electronic properties in that a CNT, based on its diameter and helicity, can either metallic or semiconducting. It is interesting to explore the coupling between the mechanical and electronic properties. Figure 15 shows sample results from a combination of molecular mechanics, dynamics, and tight binding simulations. The bandgap, normalized by the hopping parameter (3.1 eV) and a dimensionless radius R/Ro, is plotted against strain for various chiral tubes. For reference, the bandgap of a (10, 0) tube at 0% strain is 1 eV whereas the bandgap of silicon is 1.11 eV. The metallic (5, 5) tube shows no variation in bandgap under tension or compression whereas other tubes show varying degree of change. The slope itself depends on the modulus of (n-m, 3) where n and m are used to define the chirality. Within each color coded group in Fig. 15, the magnitude of the change depends on the chiral angle. For example, the bandgap changes more rapidly for a (10, 0) tube compared to a (6, 5) tube. In general, there are three transitions seen in Fig. 15. The first is metal-semiconductor transition, for example, the (9, 0) tube at 1% strain. Next, the change in bandgap with strain (slope) changes sign due to quantum number change, for example, the (10, 0) tube at 10% strain. Finally, another transition is seen when the slope changes sign again due to mechanical relaxation, for example, the (10, 0) tube at 18% strain. The critical strain, defined at the transition point due to quantum number change, varies inversely with tube diameter (not shown here) which can be verified experimentally. Further details can be found in ref. 41 which also describes the effects of torsional strain on the bandgap. Reference 42 describes the effect of bending on the electronic properties.

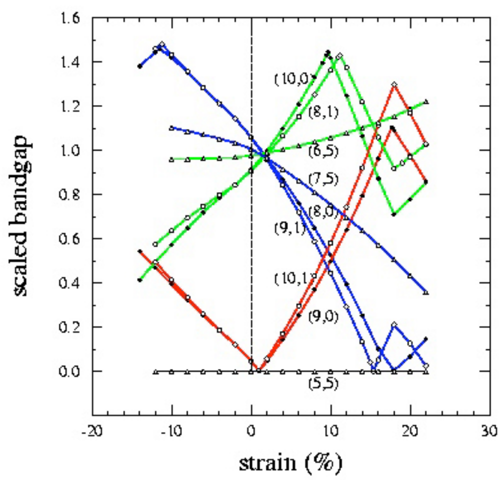


Fig. 15. Effect of strain on bandgap.
Legend: n - m = 3q + 1,
n - 3 = 3q, n - 3 = 3q - 1,
where n, m and q are integers.

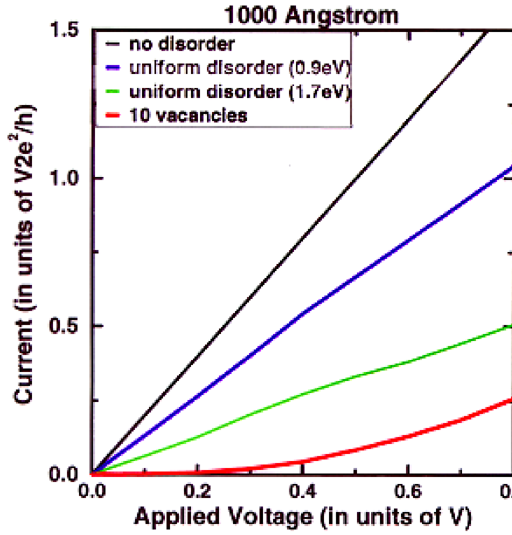


Fig. 16. Effect of disorder on CNT conductance.

A CNT is expected to be an ideal quantum wire. Ballistic transport through a nanotube would yield a low bias resistance of 6KΩ. The best measurements to date for single wall nanotubes have been shown to be in the range of 20-50 KΩ. The main reasons for the observed low conductance are defects and Bragg reflection. Theoretical work studying the effect of disorders and reflection on conductance has been carried out. Figure 16 shows computed conductance for nanotubes with uniform disorders and vacancies. Uniform disorder in CNT does not significantly affect conductance. In contrast, vacancy-type defects cause significant backscattering resulting in a conductance degradation. Further details can be found in ref. 43. Another important aspect in CNT-based electronics is the role of contacts, and theoretical investigations have been carried out to study how a carbon nanotube couples to simple metals. For good coupling, the K_f for metals must be greater than $4\pi/3a_0$ (0.17 nm^{-1} for graphite). The value of K_f for Al and Au are 1.75 and 1.21 respectively and graphite does not couple to these metals. For armchair nanotubes, this value is only 0.85$Å^{-1}$ and coupling to simple metals is very good. The armchair tube also couples better than zigzag tubes to metal. The computations show an increase in transmission with the length of the contact, as seen in experiments. Details of this study can be found in ref. 44.

The unique electronic properties of CNT have led to the fabrication of the first CNT-based field effect transistor by research groups at IBM and Delft University. The CNT-FET consisted of a SWNT in contact with source and drain contacts and modulated by a gate on the backside. The device operated at room temperature. In ref. [45], Yamada provides a theoretical analysis of the experimental data by incorporating one-dimensional quantum effects in the nanotube channel. He concludes that the lack of saturation in

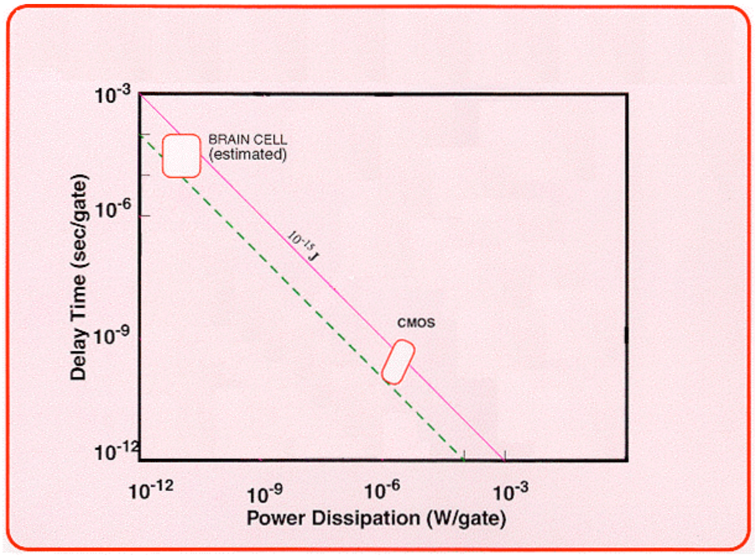


Fig. 17. Power dissipation per gate as a function of delay time

drain current as a function of drain voltage is an indication of channel carrier transport dominated by weak-localization and the electrode metal-nanotube contact influences subthreshold channel conductance vs. gate voltage. Yamada recommends a reduction in gate oxide thickness to increase the transistor gain.

While attempts to fabricate a CNT-FET are necessary first steps and allow exploration of fundamental issues and ultimate possibilities, it is critical, at this early stage, to pay attention to nanoelectronic circuit and architectures. Simple miniaturization of a CMOS-like device may not be appropriate for future nanoelectronics. Figure 17 shows switching time vs. power consumption per gate for a CMOS architecture. As device feature size and switching delay time decrease, the power consumption per gate goes up significantly and a CNT-based CMOS-like architecture is likely to face serious problems. It is interesting to note in the same plot that the brain, admittedly orders of magnitude slower, consumes significantly less power. It is possible to develop novel architectural concepts based on the unique properties of CNT, particularly metal-semiconductor, semiconductor-semiconductor, and heterojunctions [46]. Figure 18 shows nanoscale tunnel junctions for transistors which were constructed by introducing topological defects such as five (pentagon) and seven (heptagon) member rings in an otherwise all six (hexagon) based CNT [46]. Since the Y-junction proposal by Srivastava in 1997, two groups at Brown University and IISC, India independently have created Y-junctions in CVD reactors and made electrical measurements. Heterojunctions based on partial chemical functionalization and/or substitutional doping may also be possible. It is also possible to conceive of a neural tree consisting of a multiple of these Y-junctions (see Fig. 19). Deepak Srivastava envisions that these neural trees can be trained to perform complex switching and other operations just as in biological systems.

The remarkable mechanical properties of CNT are by now well known. Applications to high strength composites require extensive investigation to understand the behavior of CNT under various conditions. Nanoplasticity of SWNTs under uniaxial compression

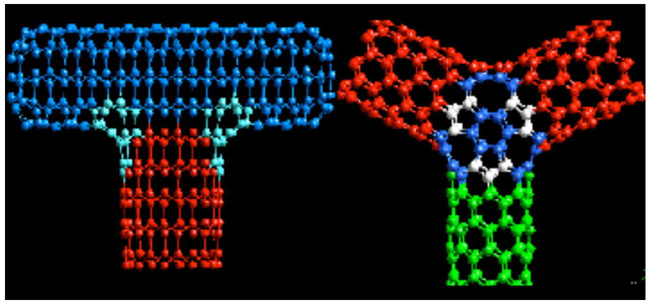


Fig. 18. Carbon nanotube "T" and "Y" junctions

was studied using generalized tight-binding molecular dynamics, and ab initio electronic structure method [47]. The bonding geometry collapses from a graphitic (sp^2) to a localized diamond like (sp^3) reconstruction under axial compression. Videoclips of this can be seen on the web under ref. [1]. The computed critical stress of about 153 GPa and the shape of the resulting plastic deformation agree well with experimental observations. Based on measurements of electrical conductivity, the thermal conductivity of SWNT has been speculated to be in the range of 1750-5800 W/m.K. which would put it in a class with CVD grown diamond. Molecular dynamics simulations at Ames has shown [48] a thermal conductivity in the range of 1000-2500 W/m.K for a (10, 10) nanotube at temperatures 100-500 deg. K. Note that this high thermal conductivity is only in the axial direction with K values in the radial direction being small. Further work is in progress to compute thermal conductivity of multiwall tubes.

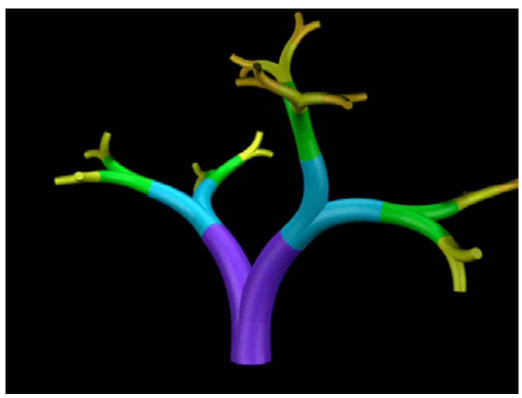
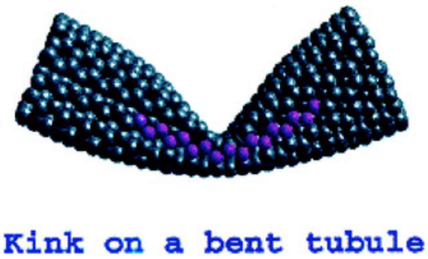


Fig. 19. Neural Tree

Several contemplated applications for CNT require functionalization of the nanotubes (both the tip and the sidewall) as mentioned earlier. Theoretical work at Ames predicts an enhanced chemical reactivity at regions of local conformational strain on the nanotubes [49]. Nanotubes which are bent or twisted show enhanced reactivity for specific sites near the distortions, as shown in Figure 20 which plots the binding energy, cohesive energy, and electronic energy for several highlighted atoms in a bent-tube. Preliminary verification of this prediction was provided by Rod Ruoff of Washington University where nanotubes laid over a V-ridge substrate were selectively attacked by nitric acid only at the sites distorted by the ridge [49].



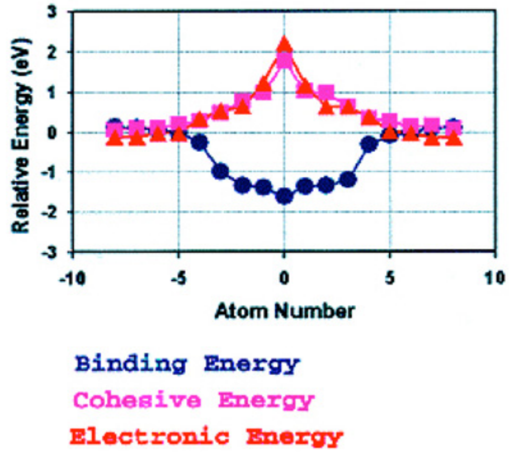


Fig. 20 Energies at various sites in a bent nanotube

The unique properties of CNT make it an attractive candidate for several nanotechnology innovations. The Ames computational nanotechnology researchers have designed a CNT-based nanogear [50, 51] shown in Fig. 21. Benzyne molecules bonded to the side of the nanotube form teeth while the nanotube forms the body about which the gear rotates. Computer simulations show that stable rotations of the driven gear are possible with the forced rotations of the powered gear. Videoclips of the nanogear rotation can be found in the website in ref. 1. The use of CNT tips in an AFM-based lithography and other applications were mentioned earlier in this report. The possibility of nanoscale etching using CNT tips has been investigated through molecular dynamic simulations. Selective atomic scale etching as well as indentation of silicon surfaces by CNT tips (mounted in an AFM) have been shown to be possible [52]. Parallelization of an array of tips has the potential to revolutionize future generation lithography. The website in ref. 1. contains videoclips of CNT etching and indentation. The possibility of storing data using H and F atoms to signify 0 and 1 bits has also been theoretically investigated [53, 54]. These atoms are sufficiently small that the interaction between adjacent data atoms on a silicon surface is small. Reference 53 speculates on how such a memory device might be constructed. A method then must be devised to differentiate

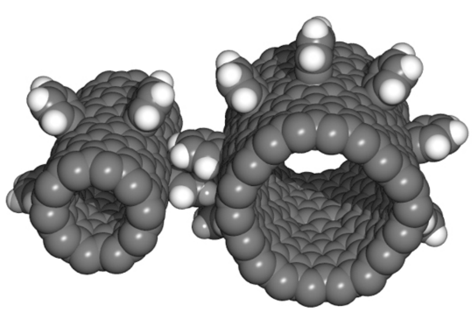


Fig. 21. A CNT-based nanogear with benzyne molecules bonded as teeth

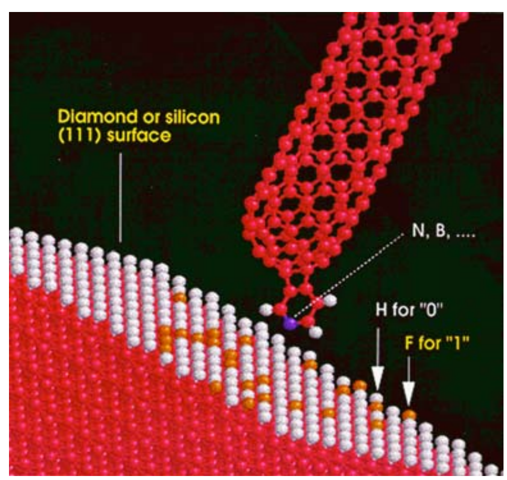


Fig. 22. Chemical data storage with H and F atoms as 0 and 1 to be read by a functionalized CNT tip.

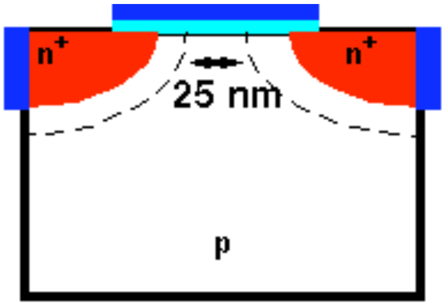
between H and F atoms unambiguously. A suggested mechanism is to have a probe that is attractive toward one atom and repulsive to the other and ref. 54 discusses the suitability of a Sc atom and electron-rich pyridine molecule as probes (to be attached to the tip of a CNT). This type of chemical storage of data is capable of 10^{15} bytes/cm^2 storage density. Parallelization of tips again can overcome speed-related problems. . In addition to CNT, the Ames group has also been investigating boron nitride nanotubes [55], for electronics and structural applications.

Computational Electronics

The main trends in device miniaturization are relentless downscaling of CMOS technology and exploration of molecular devices. Future generation smaller and faster devices are of critical importance to powerful onboard computing, autonomous "thinking" spacecraft, and petaflop computing initiative. Modeling and simulation not only provides an understanding of how these devices work, but also can serve as a design tool in developing new generation devices. In submicron devices under consideration, the electron wavelength is comparable to device dimensions and the transit time becomes comparable to scattering time. Under these conditions, classical propagators fail. The Ames Computational Electronics group has developed a multidimensional quantum device simulator based on a Nonequilibrium Green's Function (NEGF) approach. Figure 23 shows a 25 nm-MOSFET studied using this simulator along with contours of electron density.

Computational Optoelectronics

Optoelectronics is a major enabling technology for the tera-era information technology. Information transmission, processing, and storage are key areas of active research in optoelectronics. Ames has a significant computational optoelectronics activity in progress. The goal is to develop comprehensive modeling and large scale simulation capability for studying and design of quantum optoelectronics devices. Vertical cavity surface-emitting laser (VCSEL) is one of the most advanced and smallest semiconductor laser with light coming vertically out of the semiconductor wafer surface (see Fig. 24). It can be integrated with transistors in peta-flop computing with VCSEL-based optical interconnects, interprocessor communication, multi-gigabit Ethernet, high throughput image processing and virtual reality, and biological and chemical detection of molecules of interest in astrobiology and other space applications. Ames has developed a comprehensive model and simulation of VCSELs in 2-D space and time domain thus allowing detailed investigation of transverse modes. Figure 21 shows snapshots of computed laser intensity for a VCSEL. Other investigations include ultrafast modulation of semiconductor lasers [56] for high speed communication and compact and coherent THz sources [57].



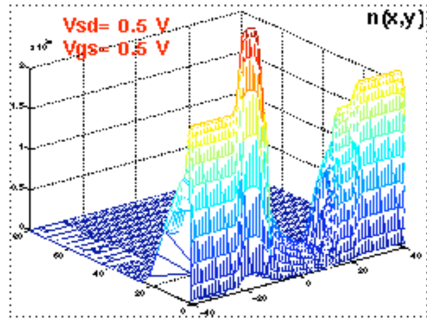
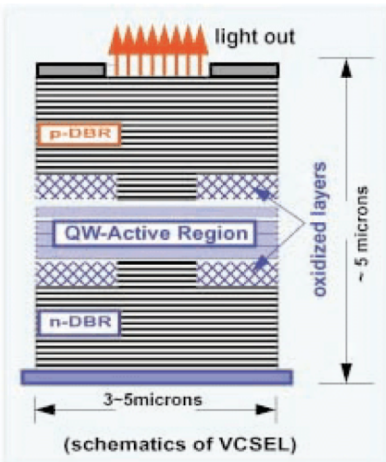


Fig. 23. Electron density contours for a 25 nm CMOS computed using a NEGF approach.



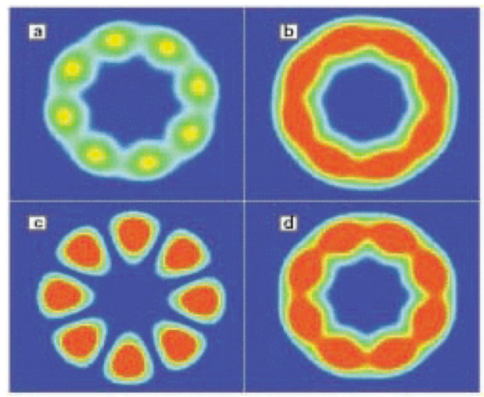


Fig. 24. 2 Dimensional VCSEL simulation showing laser intensity.

Concluding Remarks

Nanotechnology - in its various forms such as nanoelectronics, nanoelectromechanical systems, ultrasmall and highly sensitive sensors, multifunctional materials, biologically inspired materials, systems and architectures, and possibly many others scientists have not yet thought of - is expected to play a strong and critical role in future space transportation and exploration. Also, the intersection of nano, bio, and information technologies provides rich possibilities for exploring useful concepts and breakthroughs. NASA Ames Center for Nanotechnology has been conducting innovative research in these areas to meet Agency's future needs.

A strong computational program complements all experimental activities. Excellence in computational sciences has long been a tradition at Ames, and Ames organizations such as Numerical Aerodynamic Simulation (NAS) Division and Computational Chemistry Branch have led the way in numerous subjects of interest to the Agency. In that tradition, a strong program in computational nanotechnology, computational quantum electronics, and computational quantum optoelectronics is being pursued. The vision for this program is to develop highly integrated and intelligent simulation environment that facilitates the rapid development and validation of future generation of electronic, photonic, and other devices, and sensors as well as materials and processes through virtual prototyping at multiple levels of fidelity.

Acknowledgement

The authors acknowledge the excellent research contributions from the NACNT staff and the web work by Amara de Keczer. The support for the nanotechnology and biotechnology work at Ames from Scott Hubbard, Jack Boyd, Steve Zornetzer, Eugene Tu, and David Blake is gratefully acknowledged.

References

1. http://www.ipt.arc.nasa.gov
2. A. M. Cassell, S. Verma, L. Delzeit, M.Meyyappan, and J. Han, “Combinatorial Optimization of Heterogeneous Catalysts used in the Growth of Carbon Nanotubes,” Langmuir, Vol. 17, pp. 260-264 (2001).
3. A. M. Cassell, M. Meyyappan, and J. Han, “Multilayer Film Assembly of Carbon Nanotubes,” J. of Nanoparticle Research, Vol. 2, pp. 387-289 (2000).
4. L. Delzeit, B. Chen, A.M. Cassell, R. Stevens, C. Nguyen, and M. Meyyappan, “Multilayered Metal Catalyst for Controlling the Density of Single Walled Carbon Nanotube Growth,” Chemical Physics Letters vol. 348, pp. 368- (2001).
5. L. Delzeit, C.V. Nguyen, B. Chen, R. Stevens, A. Cassell, J. Han, and M. Meyyappan, "Multiwalled Carbon Nanotubes by Chemical Vapor Deposition Using Multilayered Metal Catalysts", Journal of Physical Chemistry B, Vol. 106, pp. 5629-5635 (2002).
6. H. T. Ng, B. Chen, J.E. Koehne, A.M. Cassell, J.Li, J. Han, and M. Meyyappan, "Growth of Carbon Nanotubes: A Combinatorial Method to Study the Effects of Catalysts and Underlayers," J. Phys. Chem. B, Vol. 107, pp. 8484-8489 (2003).
7. M. Meyyappan, L. Delzeit, A. Cassell and D. Hash, “Carbon Nanotube Growth by PECVD: A Review,” Plasma Sources Science and Technology, Vol. 12, pp. 205-216 (2003).
8. B.A. Cruden, A.M. Cassell, Q. Ye and M. Meyyappan, "Reactor Design Considerations in the Hot Filament/Direct Current Plasma Synthesis of Carbon Nanofibers, " J. App. Phys., Vol. 94 (6), pp. 4070-4078 (2003).
9. A.M. Cassell, Q.Ye, B.A. Cruden, J. Li, P.C. Sarrazin, H.T. Ng, J. Han, and M. Meyyappan, “Combinatorial Chips for Optimizing the Growth and Integration of CarbonNanofiber Based Devices,” Nanotechnology, Vol. 15, pp. 9-15 (2004).
10. L. Delzeit, I. McAninch, B.A. Cruden, D. Hash, B. Chen, J. Han, and M. Meyyappan, "Growth of Multiwall Carbon Nanotubes in an Inductively Coupled Plasma Reactor", Journal of Applied Physics, Vol. 91 (9), 6027-6033 (2002).
11. B.N. Khare, M. Meyyappan, J. Kralj, P. Wilhite, M. Sisay, H. Imanaka, J. Koehne, and C.W. Bauschlicher, "A Glow-discharge Approach for Functionalization of Carbon Nanotubes", Applied Physics Letters, Vol. 81 (27), p. 5237 (2002).
12. B.N. Khare, P. Wilhite, R.C. Quinn, B. Chen, R.H. Schingler, B. Tran, H. Imanaka, C.R. So, C.W. Bauschlicher Jr., and M. Meyyappan, "Functionalization of Carbon Nanotubes by Ammonia Glow-Discharge: Experiments and Modeling," J. Phys. Chem. B, Vol. 108, pp. 8166-8172 (2004).
13. B.N. Khare, P. Wilhite, and M. Meyyappan, "The Fluorination of Single Wall Carbon Nanotubes Using Microwave Plasma," Nanotechnology, Vol. 15, pp. 1650-1654 (2004).
14. B. Khare, P. Wilhite, B. Tran, E. Teixeira, K. Fresquez, D. N. Mvondo, C. Bauschlicher, Jr., and M. Meyyappan, "Functionalization of Carbon Nanotubes via Nitrogen Glow Discharge," J. Phys. Chem. B, Vol. 109, pp. 23466-23472 (2005).
15. J. Li, R. Stevens, L. Delzeit, H.T. Ng, A. Cassell, J. Han and M. Meyyappan, "Electronic Properties of Multiwalled Carbon Nanotubes in an Embedded Vertical Array", Applied Physics Letters, Vol. 81 (5), pp. 910-912 (2002).

16. J. Li, A. Cassell, L. Delzeit, J. Han, and M. Meyyappan, "Novel Three Dimensional Electrodes: Electrochemical Properties of Carbon Nanotube Ensembles", Journal of Physical Chemistry B, Vol. 106, pp. 9299-9305 (2002).
17. J. Li, H.T. Ng, A.M. Cassell, W. Fan, H. Chen, Q. Ye, J. Koehne, J. Han, and M. Meyyappan, "Carbon Nanotube Nanoelectrode Array for Ultrasenstive DNA Detection", Nano Letters, Vol. 3 (5), pp. 597-602 (2003).
18. J. Koehne, H. Chen, J. Li, A.M. Cassell, Q. Ye, H.T. Ng, J. Han, and M. Meyyappan, "Ultrasensitive label-free DNA analysis using an electronic chip based on carbon nanotube nanoelectrode arrays," Nanotechnology, Vol. 14, pp. 1239-1245 (2003).
19. T.D.B. Nguyen-Vu, H. Chen, A. M. Cassell, R. Andrews, M. Meyyappan, and J. Li, "Vertically Aligned Carbon Nanofiber Arrays: An Advance Toward Electrical-Neural Interfaces," Small, Vol. 2, 1, pp. 89-94 (2006).
20. M. Cinke, J. Li, B. Chen, A. Cassell, L. Delzeit, J. Han, and M. Meyyappan, "Pore Structure of Raw and Purified HiPCo Single-walled Carbon Nanotubes", Chemical Physics Letters, Vol. 365, pp. 69-74 (2002).
21. J.Li, Y. Lu, Q. Ye, M. Cinke, J. Han, and M. Meyyappan, "Carbon Nanotube Sensors for Gas and Organic Vapor Detection," Nano Letters, Vol. 3 (7), pp. 929-933 (2003).
22. Y. Lu, J. Li, J. Han, H.-T. Ng, C. Binder, C. Partridge, and M. Meyyappan, "Room Temperature Methane Detection Using Palladium Loaded Single-Walled Carbon Nanotube Sensors," Chem. Phys. Lett., Vol. 391, pp. 344-348 (2004).
23. J. Li, Y. Lu, Q. Ye, L. Delzeit, and M. Meyyappan, "A Gas Sensor Array Using Carbon Nanotubes and Microfabrication Technology," Electrochem. and Solid-State Lett., Vol. 8, 11, pp. H100-H102 (2005).
24. M. Cinke, J. Li, C.W. Bauschlicher, A. Ricca, and M. Meyyappan, "CO_2 Adsorption in Single-Walled Carbon Nanotubes," Chem. Phys. Lett., Vol. 376, pp. 761-766 (2003).
25. C.V. Nguyen, K.J. Chao, R.M.D. Stevens, L. Delzeit, A. Cassell, J. Han and M. Meyyappan, “Carbon Nanotube Tip Probes: Stability and Lateral Resolution in Scanning Probe Microscopy and Applications to Surface Science in Semiconductors,"
26. R. Stevens, C. Nguyen, A. Cassell, L. Delzeit, M. Meyyappan, and J. Han, “Improved Fabrication Approach for Carbon Nanotube Probe Devices,” Applied Physics Letters, Vol. 77 (21), pp. 3453-3455 (2000).
27. R.M. Stevens, C.V. Nguyen, and M. Meyyappan, "Carbon Nanotube Scanning Probe for Imaging in Aqeous Environment," IEEE Transactions on Nanobioscience, Vol. 3 (1), pp. 56-60 (2004).
28. P. Sarrazin, "Field Emission" in Carbon Nanotubes: Science and Applications, Ed: M. Meyyappan, CRC Press, Boca Raton, FL (2004).
29. J. Li, Q. Ye, H.T. Ng, A. Cassell, R. Stevens, J. Han and M. Meyyappan, “A Bottom-up Approach for Carbon Nanotube Interconnects,” Applied Physics Letters, Vol. 82, pp. 2491-2493 (2003).
30. Q. Ngo, D. Petranovic, S. Krishnan, A.M. Cassell, Q. Ye, J. Li, M. Meyyappan, and C.Y. Yang, "Electron Transport Through Metal-Multiwall Carbon Nanotube Interfaces," IEEE Transactions on Nanotechnology, Vol. 3 (2), p. 311 (2004).

31. Q. Ngo, B.A. Cruden, A.M. Cassell, G. Sims, M. Meyyappan, J. Li, and C.Y. Yang, "Thermal Interface Properties of Cu-filled Vertically Aligned Carbon Nanofiber Arrays," Nano Letters, Vol. 4 (12), pp. 2403-2407 (2004).
32. H.T. Ng, B. Chen, J. Li, J. Han, M. Meyyappan, J. Wu, S.X. Li, and E.E. Haller, "Optical Properties of Single-Crystalline, ZnO Nanowires on M-Sapphire," Applied Physics Letters, Vol. 82, pp. 2023-2025 (2003).
33. H.T. Ng, J. Li, M.K. Smith, P. Nguyen, A. Cassell, J. Han, and M. Meyyappan, "Growth of Epitaxial Nanowires at the Junctions of Nanowalls," Science, Vol. 300, pp. 1249 (2003).
34. P. Nguyen, H.T. Ng, J. Kong, A.M. Cassell, R. Quinn, J. Li, J. Han, M. McNeil, and M. Meyyappan, "Epitaxial Directional Growth of Indium-Doped Tin Oxide Nanowire Arrays", Nano Letters, Vol. 3 (7), pp. 925-928 (2003).
35. P. Nguyen, H.T. Ng, and M. Meyyappan, "Growth of Individual Vertical Germanium Nanowires", Advanced Materials, Vol. 17 (5), pp. 549-553 (2005).
36. A. Mao, H.T. Ng, P. Nugyen, M. McNeil, and M. Meyyappan, "Silicon Nanowire Synthesis by a Vapor-Liquid-Solid Approach," Journal of Nanoscience and Nanotechnology, Vol. 5, pp. 831-835 (2005).
37. P. Nguyen, H.T. Ng, and M. Meyyappan, "Catalyst Metal Selections for the Synthesis of Inorganic Nanowires," Advanced Materials, Vol. 17, pp. 084311-1 - 084311-11 (2005).
38. S. Vaddiraju, A Mohite, A. Chin, M. Meyyappan, G. Sumanasekera, B.W. Alphenaar, and M.K. Sunkara, "Mechanisms of 1D Crystal Growth in Reactive Vapor Transport: Indium Nitride Nanowires", Nano Letters, Vol. 5, 8, pp. 1625-1631 (2005).
39. P. Nguyen, H.T. Ng, T. Yamada, M.K. Smith, J. Li, J. Han, and M. Meyyappan, "Direct Integration of Metal Oxide Nanowire in Vertical Field-Effect Transistor," NanoLetters, Vol. 4 (4), pp. 651-657 (2004).
40. H.T. Ng, J. Han, T. Yamada, P. Nguyen, Y.P. Chen, and M. Meyyappan, "Single Crystal Nanowire Vertical Surround-Gate Field-Effet Transistor," Nano Letters, Vol. 4 (7), pp. 1247-1252 (2004).
41. L. Yang, M. Anantram, J. Han, and J.P. Lu, "Band-gap Change of Carbon Nanotubes: Effect of Small Uniaxial and Torsional Strain", Physical Review B, Vol. 60(19), pp. 13874-13878 (1999).
42. L. Yang and J. Han, "Electronic Structure of Deformed Carbon Nanotubes", Physical Review Letters, Vol. 85 (1), pp. 154-157 (2000).
43. M.P. Anantram and T.R. Govindan, "Conductance of Carbon Nanotubes with Disorder: A Numerical Study", Physical Review B, Vol. 58 (8), pp. 4882-4887 (1998).
44. M. Anantram, S. Datta, and Y. Xue, "Coupling of Carbon Nanotubes to Metallic Contacts", Physical Review B, Vol. 61 (20), pp. 14219 (2000).
45. T. Yamada, "Analysis of Submicron Carbon Nanotube Field Effect Transistors," Applied Physics Letters, Vol. 76 (5), pp. 628-630 (2000).
46. M. Menon and D. Srivastava, "Carbon Nanotube "T-junctions": Nanoscale Metal-Semiconductor-Metal Contact Devices", Physical Review Letters, Vol. 79, pp. 4453-4456 (1997).
47. D. Srivastava, M. Menon, and K. Cho, "Nanoplasticity of Single-wall Carbon Nanotubes Under Uniaxial Compression,"Physical Review Letters, Vol. 83 (15), pp. 2973-2976 (1999).

48. M.A. Osman and D. Srivastava, "Temperature Dependence of Thermal Conductivity in Single Wall Carbon Nanotubes", Applied Physics Letters (2000).
49. D. Srivastava, D.W. Brenner, et al, "Prediction of Enhanced Chemical Reactivity at Regions of Local Conformational Strain on Carbon Nanotubes: Kinky Chemistry" Journal of Physical Chemistry, B., Vol. 103, pp. 4330-4337 (1999).
50. J. Han, A. Globus, R. Jaffe and Glenn Deardorff, "Molecular Dynamics Simulation of Carbon Nanotube Based Gears", Nanotechnology, Vol. 8, pp. 95-102 (1997).
51. D. Srivastava,"A Phenomenological Model of the Rotation Dynamics of Carbon Nanotube Gears with Laser Electric Fields", Nanotechnology, Vol. 8, pp. 186-192 (1997).
52. F. Dzegilenko, D. Srivastava, and S. Saini, "Nanoscale Etching and Indentation of Silicon (111) Surface with Carbon Nanotube Tips", Nanotechnology, Vol. 10, p. 253 (1999).
53. C.W. Bauschlicher, A. Ricca, and R. Merkle, "Chemical Storage of Data", Nanotechnology, Vol. 8, pp. 1-5 (1997).
54. C.W. Bauschlicher and M. Rosi, "Differentiating Between H or F and CN on C(111) of Si(111) Surfaces", Journal of Physical Chemistry B, Vol. 102, pp. 2403-2405 (1998).
55. M. Menon and D. Srivastava, "Structure of Boron Nitride Nanotubes: Tube Closing Versus Chirality", Chemical Physics Letters, Vol. 307, pp. 407-412 (1999).
56. C.Z. Ning, S. Hughes, and D.S. Citrin, "Ultrafast Modulation of Semiconductor Lasers Through a Terahertz Field, "Applied Physics Letters, Vol. 75 (4), pp. 442-444 (1999).
57. A. Liu and C.Z. Ning, "Terahertz Optical Gain Based on Intersubband Transitions in Optically Pumped Semiconductor Quantum Wells: Coherent Pump-Probe Interactions," Applied Physics Letters, Vol. 75 (9), pp. 1207-1209 (1999).