SYMPOSIUM Z
Making Functional Materials with Nanotubes
November 26 - 29, 2001

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487
10:15 AM **2.1.4**

**CARBON NANOTUBE FIBERS.** Brigitte Vigolo, Philippe Paulin, Caroline Zocca, Helene Richard, Centre de Recherche Paul Sabatier-CNRS, Pessac, FRANCE; Patrick Bernier, GDPC, Montpellier, FRANCE; Pascale Linaoco, LPS, Univ Paris Sud, FRANCE.

Carbon nanotubes can be processed into long fibers using a simple spinning-like process. The method consists in dispersing the nanotubes in a surfactant solution, re-condensing the nanotubes in the flow of a coagulating polymer solution to form a nanotube mesh, and then calibrating this mesh to a nanotube fiber. We discuss in this paper the main features of the process and its optimization for different types of nanotubes. Structural characteristics and physical properties of carbon nanotube fibers will be also presented. Although far from being fully optimized, we believe that already obtained fibers are potentially useful in different applications such as sensors and actuators. In addition, carbon nanotube fibers can be modified and improved in different ways using mechanical, chemical, or thermal treatments. We present preliminary results along these approaches. We hope that the simplicity of the present method and the practical use of fibers for integrating nanotube fibers in devices and materials will contribute in the future in making carbon nanotube fibers more suitable for potential applications.

10:45 AM **2.1.5**

**TOWARDS BUILDING THREE DIMENSIONAL ARCHITECTURES OF CARBON NANOTUBES.** D.Q. Wei, Y. Jung, R. Vajtai, G. Ramirez, P.M. Ajayan, Rensselaer Polytechnic Institute, Department of MSE, Troy, NY.

It is important to develop 3D and 3D architectures of nanotubes for several applications such as field emission displays, electronic circuits, and sensor arrays. This problem mandates achieving control on the nucleation sites and growth directions of nanotubes on pre-defined planar substrate surfaces. Based on our previous work of growing aligned carbon nanotubes selectively on SiO$_2$/Si patterns, we report that we can now build 3D architectures of carbon nanotubes controllably and reproducibly on such substrates. By combining standard microfabrication techniques and chemical vapor deposition, we demonstrated the direct growth of nanotubes to produce vertically and horizontally aligned nanotube arrays, ordered fibers and structures with complex geometry and shapes. Such architectures inherit the position, shape and the size of the original patterns on the substrates and therefore, can be controlled with relative ease.

11:00 AM **2.1.6**

**MICRO-PATTERNCED VERTICALLY WELL-ALIGNED CARBON NANOTUBE GROWTHS ON THE PLANE Si OR INSIDE THE TRENCHES.** Jung Inn Sohn, Seonghoon Lee, Kwangju Institute of Science and Technology (K.I.S.T.), Department of MSE, Kwangju, KOREA; Yeon Ho Song, Sung-Yool Choi, Jin Ho Lee, Young-Hi Kang, ETRI, Micro- Electronics Tech. Labs., Taejon, KOREA.

The good field emission property of carbon nanotubes coupled with their high mechanical strength, chemical stability, and high aspect ratio, is ideal in building efficient and inexpensive field emission electronic devices. The fabrication process we suggest here will be of great help in developing an integrated radio frequency (RF) amplifier or field emission-controllable cold electron guns for field emission displays (FEDs). This fabrication process is compatible with present semiconductor processing technologies. We grow micro-patterned vertically well-aligned carbon nanotubes on the plane Si surface or inside the trenches in the first time, using chemical vapor deposition (CVD), photolithography, pulsed laser deposition (PLD), reactive ion etching (RIE), and lift-off methods. In detail, we grow carbon nanotubes on the plane Si(100) substrate with a pattern of squares of 50µm by 50µm, 10µm by 10µm, or 5µm by 5µm. We also fabricate the simple and the most desirable triode-type field emitting electronic device containing carbon nanotube field emitters in a trench of 10µm deep and 6µm wide as cold cathode. This fabrication process can be widely applied for developments of electronic devices using carbon nanotube field emitters as cold cathodes and revolutionize field emitting electronic devices.

11:15 AM **2.1.7**

**FORMATION OF ALIGNED SINGLE-WALL CARBON NANOTUBE BUNDLES BY SELF-ASSEMBLY.** H. Shimoda, I. Fleming, K. Horton and O. Zhou, University of North Carolina, Chapel Hill, NC.

We report the formation of freestanding membranes containing aligned single-wall carbon nanotube (SWNT) bundles by self-assembly. Purified SWNTs were chemically etched to short bundles by ultrasonic-assisted oxidation. The processed SWNTs were dispersed in de-ionized water and were let to settle overnight at room temperature. Rectangular shape membranes (~4 x 10mm) were found to float on the water surface. Transmission electron microscopy...
measurements show that the SWNT bundles are initially aligned and randomly spaced within the membrane. These results suggest that the short SWNT bundles exhibit nematic liquid crystal behavior.

11:30 AM Z1.8
GROWTH OF ALIGNED CARBON NANOTUBE ARRAYS WITH CONTROLLED SITE DENSITY BY ELECTROCHEMICAL DEPOSITION. Yi-Tu, Zhengping Huang, Denzi Wang, Joel Moser, Michael Naughton, Zhifang Ren, Boston College, Dept of Physics, Chestnut Hill, MA.

Electrochemical deposition has been used to prepare nickel nanoparticles as catalyst for growth of well-aligned carbon nanotube arrays with controlled site density. The catalyst particle size and density are controlled by the combining effect of concentration of the solution, amplitude of the pulse current, and the pulse length. With these particles, well-aligned carbon nanotube arrays with site density as low as $10^{10}$ sites per cm² by plasma-enhanced chemical vapor deposition (CVD) method have been achieved. The low density is absolutely necessary for good field emission for flat panel display devices.

11:45 AM Z1.9
DIAMETRIC-CONTROLLED GROWTH OF CARBON NANOTUBES. Chiu Li, Cheng, Andrea Kurtz, Hongjun Park and Charles M. Lieber, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA.

Carbon nanotubes have many interesting electrical, chemical and mechanical properties. Nanotubes with varying diameters are beneficial for the development of theoretical and practical applications such as hydrogen storage, nano-electrochemical devices and atomic force microscopy (AFM) probes. Here we report the synthesis of carbon nanotubes with controlled-diameter using nanosized iron decorated carbon black as catalyst for chemical vapor deposition (CVD). To eliminate electron microscopy and atomic force microscopy studies of the carbon nanotubes grown from iron collod of 3, 7 and 12nm diameter arrays produced by solution-phase showed that single-walled carbon nanotubes and thin-walled multi-walled carbon nanotubes with 7, 12 and 12nm diameters, respectively, can be synthesized. As the size of the starting catalyst particles increases, an increase in flux of hydrogenation reactions is required for the growth of carbon nanotubes with similar diameters as those of the catalyst. High CVD temperature was found to increase the crystallinity of as-grown carbon nanotubes. Applications using this method for fabrication of carbon nanotube AFM probes will be discussed.

SESSION 22 PROGRESS IN SYNTHESIS AND PROCESSING II

Chairs: Masa Yumura and David B. Geoghegan
Monday Afternoon, November 26, 2001

130 PM Z2.1
LASER PRODUCTION OF SINGLE-WALL CARBON NANOTUBES OF SPECIFIC SIZE AND TYPE BY VARIATION IN PEAK PULSE POWER. Anne Dillon, Jeff Allman, Kim Jones, Philip Pasilla, Thomas A. Hicken, National Renewable Energy Laboratory, Golden, CO; Thomas Gennett, Rochester Institute of Technology, Rochester, NY.

Carbon single-wall nanotubes (SWNTs) have diameters that may vary from ~0.8 - 2.7 nm and depending on tube chirality are either semiconducting or metallic. For certain of the many potential nanotube applications it will be important to develop methods for the controlled production of specific sizes and types of SWNTs. For example, the large-scale fabrication of nanotube based devices will depend on the assembly of very specific nanotubes. It has also been recently been suggested that single- and multi-conducting nanotubes are desirable for the optimization of nanotube hydrogen storage properties. Here we demonstrate that for a laser vaporization process at a constant synthesis temperature of 1200°C, the diameter distributions of both the semi-conducting and the metallic SWNTs may be tailored through variation in peak power. In each case smaller diameter nanotubes are produced with increasing peak power. It is also possible to regulate the concentrations of semi-conducting or metallic tubes by varying the peak pulse power during synthesis. In this case, larger peak powers result in the production of semi-conducting SWNTs at a much higher density. However, we find that overall nanotube yields are increased for lower peak pulse powers where a vaporization regime is more naturally maintained. Nanotube microwave power of 1.525 W/cm² contain predominantly semi-conducting tubes, but the overall SWNT content may be lowered by as much as a factor of three compared to materials produced at lower peak powers.


1:45 PM Z2.2
CONTROLLED DIMENSIONAL OF NANOMETER FILMS FROM 5 - 300 NANO METERS. MP. Siegel, D. L. Overmyer, PP. Provencio, and F. H. Kuester, Sandia National Laboratories, Albuquerque, NM; N. J. DiNardo, Drexel University, Dept of Physics, Philadelphia, PA.

We grow multiwall carbon nanotube films using thermal CVD at atmospheric pressure from a mixture of acetylene and nitrogen. Nanotube outer (inner core) diameters, ranging from 5 - 300 nm (2 - 15 nm), are controlled primarily by growth temperature, which varies from 600 - 780°C respectively. Growth at lower temperatures yields poor carbon structures, growth at higher temperatures yields a micron-sized diameter tubular-like cluster structures from the gas phase, independent of the catalyst, that coats the inside of the furnace apparatus. These films are then grown on Si(100) using 4 mm thick spun coated Ni as the catalyst and 80°C prevents silicidation. We reduce the Ni/WSi(100) substrates in flowing CO at 600 C for 1 hour, raise the temperature to that desired for growth in N, and then expose the samples to the growth environment for 15 minutes. Samples with no-no in nitrogen. Nanotube formation is extremely uniform over the entire sample area. We will present detailed microscopy studies, both SEM and TEM, of nanotube structural properties, and AFM of the Ni catalyst layer morphology following various stages of the growth process. We will show that nanotube diameters are not solely dependent upon the Ni/catalyst grain size, but also are a function of growth time. These experiments define nanotube growth conditions which will be applied to the use of nanotube templates for organic devices and as pre-determined pinhole structures for optimal growth of aligned multiwalled carbon nanotube arrays.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. DOE under contract DE-AC04-94AL85000.

2:00 PM Z2.3
Boron Nitride Nanotubes: Nanocone and NanoCable. Yoshio Honda, Domeni Golberg, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, JAPAN.

The boron nitride nanotubes, nanowires, and nanocables have been prepared and their atomic structures are identified by using a 300kV filed emission transmission electron microscopy with the use of electron energy loss spectroscopy. Multi-walled BN nanotubes were prepared by the substitution reaction, where carbon nanotubes are heated with boron oxides at temperatures of 1500°C under N₂ gas. C nanotubes were converted to BN nanotubes without a drastic change of morphology. The addition of catalytic oxides of Mg-O3 increased a yield of pure BN nanotubes. It is shown that BN nanotubes have a preferential zigzag orientation. The bamboo-like BN nanowires having a rhombohedral at packing were found. An efficient CVD synthetic route for bulk quantities of BN nanotubes was also developed, where a uniform BN precursor was used. BN nanowires consist of siened wall approximately 10 nm in width separated by thin empty core (diameter 1nm). The observed apex angles were close to 35°, which can be explained by a model of orderly stacked 24h-pitch. Some of the nanotubes of 300 degree disconnections was found, implying that the structure containing line defects of non-BN bonds may form. The first synthesis of insulating BN nanotubes was successfully carried out, where BN nanotubes were continuously filled with Fe/Ni alloy. The filled nanotube diameters ranged between 30 to 300nm, whereas the filled length of the nanotubes reached several microns.

2:30 PM Z2.4

Boron nitride nanotubes (BN-NTs) are attracting considerable interest due to their unique physical properties which make them a possible alternative to their carbon brethren in regards to possible applications. However, until recently, careful study of BN-NTs has been hampered by the paucity of material produced by various synthesis methods which has prevented the realization of certain experiments. Here, a new route to the successful synthesis of single wall boron nitride nanotubes (BN-NTs) in large quantities is presented. It is based on the vaporization of a BN (or boron target) by a continuous CO2 laser under nitrogen atmosphere [1]. High-resolution transmission electron microscopy (HRTEM) analysis has shown the synthesis product to be composed of almost exclusively single-wall boron nitride nanotubes (BN-SWNTs) either isolated or organized in
ropes. Furthermore, very high resolution images has revealed that the majority of BN-SWNTs seem to have a zig-zag configuration. The chemical treatment of the tubes yields hydrocarbon and energy loss spectroscopy (EELS) analysis which also determined that BN-SWNTs are capped by a boron particle; strongly supporting a root-based growth mechanism with tubes growing from boron nanoparticles issued from the target. These results are particularly interesting as they represent the first time that BN-SWNTs have been synthesized in quantities and quality comparable to that of carbon nanotubes with the advantage that no catalyst is needed. First characterization results of the BN-SWNTs will be presented. [1] R. Lee et al., Phys. Rev. B (2001), in press.

3:30 PM 22.5
PURIFICATION AND DIAMETER-DEPENDENT OXIDATIVE STABILITY OF SWNT SYNTHESIZED BY THE HIGH PRESSURE CARBON MONOXIDE PROCESS. Wei Zhao, Yee Hau Ooi, Richard Rasou, Brian W. Smith, Srinivasan Chandrasekhar, Peter Pagliaro, David E. Larson, John E. Fischer, University of Pennsylvania, Dept. of Materials Science, Philadelphia, PA; Richard J. Bronikowski, Peter A. Willis, and Richard E. Smalley, Rice University, Center for Nanoscale Science and Technology, Houston, TX.

Low T oxidation followed by brief sonication in hot HCl has been optimized to remove Fe catalyst residues from HPCO material with minimal loss of SWNTs. TGA shows that one pass reduces the Fe catalyst content from typically 0.10 ± 0.06 to 0.16 to 0.18 ± 0.02 by weight, most of which corresponds to Fe removal. In one case, a second pass reduced Fe content from 0.16 to 0.04 wt%. Raman scattering reveals a broad diameter distribution with a peak at 1.04 ± 0.1 nm. Neutron diffraction and HRTEM show a low degree of microcrystalline tube formation compared to laser ablation and carbon arc methods. Neither of these attributes are affected by purification or vacuum annealing. Fe catalyzed synthesis of SWNT; higher oxidation temperatures can be used after the first pass without significant loss of tubes. After purification we find excellent correlation between TGA and Raman data, showing that [oxidation] varies inversely with tube diameter. This can be explained by the larger strain associated with greater curvature of small tubes. HRTEM shows that the remaining tubes are intact with clean sidewalls, so controlled burning can be used to narrow the diameter distribution by burning off small-diameter tubes.

3:45 PM 22.6

Total exclusion of entrapped catalytic impurities from single wall carbon nanotubes (SWNTs) has thus far remained elusive. Currently, the purification procedures have a high catalyst incorporation (>40 wt%; as monitored by EDAX), which drastically decreases its thermal stability and processability, thereby eliminating it from many of the proposed applications intended for nanotubes. A novel catalytic carbon purification process leading to complete elimination of the metallic impurities and applicable to both laser ablated and HPCO produced nanotubes will be presented. The above multi-step purification process involving a combination of brief room temperature sonication and vacuum annealing at > 900 °C results in the complete elimination of these [metallic, catalytic] impurities. Following purification, HRTEM of the nanotubes shows no metallic impurities, while XRD and Raman spectroscopy indicate high quality and purity of the nanotubes. The present purification method is time and cost effective and applicable to SWNTs produced by any of the current manufacturing processes.

4:00 PM 22.7

While there have been many advances in single-walled carbon nanotubes (SWNT) synthesis, most recently the HPCO process, there still remains the difficult task of separating the SWNTs from amorphous carbon and catalyst impurities contained within the graphite shells. Many potential purification methods, such as acid treatment and air oxidation, have been explored with the key obstacles produce inconsistent results due to the inhomogeneous morphology of SWNTs. As well, these treatments have not been studied extensively in terms of how the SWNT surface has been chemically modified. In this discussion, we explore the transmission electron microscopy (HRTEM) to qualitatively determine the purity of the SWNTs. The thermal oxidation of SWNTs, as well as residual catalyst content, is determined by Thermogravimetric Analysis (TGA). Infrared and Raman spectroscopy are used to determine the carbon content in the purified SWNTs, as well as changes in the SWNT surface induced by the purification treatment. The effects of vacuum annealing over a significant temperature range on SWNT defects are also explored.

4:15 PM 22.8

Single-walled carbon nanotubes (SWNTs) are often produced as a minority constituent in the reaction product. Also present, for example, are amorphous carbon which occurs the bundles walls, residual metal catalyst, and multi-shell carbon which covers the metal residue. Fundamental studies and proposed applications of SWNTs require reasonably pure material. It is a challenging problem to separate the reaction product and remove the catalyst. In the present work, we show that local heating of the carbon-encapsulated metal catalyst particles in air using microwave radiation is a very beneficial first step in general purification scheme for SWNTs. The local microwave heating, either as a direct carbon coating, or in expansion of the metal core, weakens the carbon overcoating, allowing a mild acid treatment at low temperature to remove most, if not all, of the residual metal catalyst. Transmission electron microscopy, oxidation analysis, energy-dispersive X-ray and Raman spectroscopy data are presented which reveal the benefits of the microwave processing SWNT material.

4:30 PM 22.9
MACROSCOPIC SHEET ASSEMBLIES OF MAGNETICALLY ALIGNED CARBON NANOTUBES PRODUCED IN MAGNETIC FIELDS. Michael J. Cumming, Daron A. Walters, Richo Scutieron, Richard E. Smalley, Rice University, Houston, TX; R. Hagemann, J. Viare, and J. E. Fischer, University of Pennsylvania, PA.

Macroscopic samples of highly aligned SWNTs have been produced by filtration in the presence of a magnetic field. A 25 Tesla vertical bore magnet and 7 Tesla horizontal bore magnet were aligned. Alignment resulted from the difference in magnetic susceptibility between nanotubes parallel and perpendicular to the field. The presence of domains resulting from filtration exhibit anisotropic mechanical and optical properties. Unlike similar mica composites of unsorted material, the aligned mica is aligned preferentially along the magnetic field axis, the axis is consistent with a line of rolling fibers perpendicular to this axis. Micro-Raman scattering showed a factor of 10-100 difference in signal intensity for orientations parallel and perpendicular to the polarization of incident radiation. This process produces aligned nanotubes in the form of free-standing, 15 cm wide, (13.5 ± 1.5 cm long, and 10 microns thick. This promises to provide a more practical approach to achieving macroscopic aligned assemblies of nanotubes, further potential applications.

4:45 PM 22.10
EPOXY REINFORCEMENT USING POLYMER WRAPPED SINGLE WALLED CARBON NANOTUBES. Richard A. Bley, Daniel Benczechen, Jennifer F. Clark, James P. Scott, Eron Research, Boulder, CO.

We are developing a method for incorporating Single Walled Carbon Nanotubes (SWNT) into epoxy thermosets to act as reinforcement. The helical structure of poly(methylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene) (PMV) encourages this polymer to wind itself around both individual SWNTs and multiple SWNT ropes. This forms a polymer/nanotube composite which is mechanically mchored to the nanotube but is not chemically bound.
to it. Because interaction between the PmPV and SWNTs is purely mechanical, no incursion into the bond structure of the SWNTs occurs. Placing functional groups on the side chains of the PmPV polymer will make covalent bonding possible between this PmPV derivative and the epoxy matrix in the final composite. This will provide optimal strength in the final composites by maximizing the load transfer properties of the derivative. How well this final composite is capable of conveying the extraordinary strength and durability of the carbon nanotubes to the final PmPV/SWNT/epoxy composite as a whole will depend on the PmPV derivatives ability to transfer the applied load from the composites epoxy matrix to the SWNTs.

SESSION 23: POSTER SESSION
SYNTHESIS, PROCESSING, AND POLYMER
COMPOSITES
Monday Evening, November 26, 2001
8:00 PM
Exhibition Hall D (Hynes)

23.1
CONTROLLED SYNTHESIS OF CARBON NANOSTRUCTURES WITH CYLINDER-ON-CONE SHAPE. Vladimir I. Merkulov, Instrumentation and Controls (I&C) Division, Oak Ridge Natl Laboratory, Oak Ridge, TN; Anuradha S. Melechko, Center for Environmental Biotechnology, University of Tennessee, Knoxville, TN; Douglas H. Lowndes, Solid State Division, Oak Ridge Natl Laboratory, Oak Ridge, TN; Michael A. Guillen and Michael L. Simpson, Dept of Electrical and Computer Engineering, University of Tennessee, Knoxville, TN; and I&C Division, Oak Ridge Natl Laboratory, Oak Ridge, TN.

The ability to control the nanoscale shape of carbon nanostuctures in a large-scale synthesis process is reported for the first time. Utilizing electron beam lithography and plasma-enhanced chemical vapor deposition (PECVD), nanoscale carbon tips with conical and cylinder-on-cone shapes were fabricated. The transition between the cylindrical and conical carbon nanosstructures was controlled by changing the growth parameters during the PECVD process. In contrast to simple conical or cylindrical tips, the cylinder-on-cone nanotips possess both mechanical stability and the high aspect ratio needed for use in nanoelectronics, nanomechanics, and emission devices, biological probes, and other nanoscale devices. Since the growth process is highly deterministic in allowing large-scale synthesis of precisely engineered nanoscale components only at selected locations, the technique reported here provides an important tool for a practical nanotechnology.

23.2
NANOTUBES OF SINGLE CRYSTALLINE TELLURIUM: SYNTHESIS, CHARACTERIZATION, AND UTILIZATION. Brian Myers, Younan Xia, Dept of Chemistry, University of Washington, Seattle, WA.

We have recently demonstrated a new approach based on concentration depletion at seeds for the large-scale synthesis single-crystalline nanotubes of trigonal tellurium. The diameters of these nanotubes can be controlled in the range of 10-200 nm, with their lengths up to tens of micrometers. By varying the reaction conditions, these nanotubes could also be changed into nanorods with well-controlled diameters at least 100 nm. In this talk, we will discuss the growth mechanism (as revealed by SEM and TEM studies), and some applications for these metallic nanotubes.

23.3
GROWTH OF SINGLE-WALLED CARBON NANOTUBES IN A CONDENSED PHASE. Rajib Sen, Shinzo Suzuki, Takayuki Taniaki, Yoshi Achiwa, Tokyo Metropolitan Univ, Dept of Chemistry, Tokyo, JAPAN; Hiroshi Oku, Tokyo Metropolitan Univ, Dept of Physics, Tokyo, JAPAN.

Single-walled carbon nanotubes (SWNTs) were grown from the soot prepared by laser ablation of metal-carbon composite target at 550°C and 700°C in a condensed phase using post-annealing technique. It was found that the soot prepared only by laser ablation at such low ambient temperature did not contain SWNTs, while post-annealing of that soot at 1200°C in Ar gas atmosphere resulted in the formation of SWNTs. Interestingly, the soot prepared at room temperature and 400°C did not show any indication of SWNTs, even after post-annealing procedure. These experimental findings strongly suggest that the nucleation sites for the growth of SWNTs can be formed above a certain threshold ambient gas temperature (around 550°C), and the existence of these sites are required for the growth of SWNTs from the metal-carbon mixture in a condensed phase by post-annealing procedure.

23.4
THE CATALYTIC EFFECTS OF COBALT AND COBALT SILICIDE ON CARBON NANOTUBE FORMATION. Hui Lin Chang, Chao Han Lin, Cheng Tsai Kuo, Department of MSE, National Chiao Tung University, Hsinchu, TAIWAN.

The cobalt was widely used as catalyst for nanotube growth on Si substrate. However, very few researchers were able to determine the differences in catalytic behaviors between Co and CoSi. In this study, the cobalt nanotubes were grown on Si substrate by MPCVD method using a mixture of CH₄ and H₂ as source gases. The substrate was covered by four different films before nanotube growth, i.e. (1) Co, (2) SiO₂ and then Co, (3) CoSi, and (4) chemically etched CoSi films. The preliminary results showed that the average nanotube diameters for four different substrate pretreatments under the same deposition conditions are about 18 nm, 100 nm, 40 nm and 10 nm, respectively. The pretreatment (3) indicates the best performance in terms of emission. In this case, the turn-on voltage can be as low as 4.6 V/μm, and the emission current density can reach 5 mA/cm² at 10 V/μm. The preliminary results also reveal that the catalysts of Co and Si are most effective at different pretreatments [1] and [2] may be due to different kinds of interaction of Co and Si to form CoSi. The differences in catalytic effects between pretreatments [1] and [2] may be due to different kinds of interaction of Co and Si to form CoSi. The preliminary results also reveal that the catalysts of Co and Si are most effective. The different kinds of interaction of Co and Si to form CoSi. The preliminary results also reveal that the catalysts of Co and Si are most effective.

23.5
PREPARATION OF SINGLE-WALLED CARBON NANOTUBES BY MULTISTEP LASER ABABLATION OF TWO KINDS OF TARGET. Shinzo Suzuki, Rajib Sen, Takayuki Taniaki, Yoshi Achiwa, Tokyo Metropolitan Univ, Dept of Chemistry, Tokyo, JAPAN; Hiroshi Oku, Tokyo Metropolitan Univ, Dept of Physics, Tokyo, JAPAN.

Single-walled carbon nanotubes (SWNTs) were prepared by simultaneous laser ablation of graphite target and metal/Alloy target inside a furnace at 1200°C in ambient temperature mixed with Ar gas atmosphere. Each target was vaporized with a different laser, respectively. Various metal targets (Ni, Co, Fe, and permalloy) were tested in order to find the difference in the resulting SWNT yield. At the moment, it seems to reveal the highest yield for the SWNT formation. Also, time-resolved images of the plume by carbon and metal species after laser vaporization were collected using a high-speed video camera. These images suggest that the hot plumes due to carbon and metal species do not mix together so extensively, at least in about half a second after laser vaporization. Based on these experimental findings, a plausible growth mechanism for SWNTs is presented and discussed.

23.6
GROWTH OF HIGHLY ORDERED CARBON NANOTUBE ARRAYS ON SILICON SUBSTRATE USING POROUS ALUMINA FILTER PATTERN NANO-TEMPLATE. Chen, Weicheng, Hang, Yong, Gong, Peidong Kihanga, and Greg A. Grimes, Univ of Kentucky, Dept of Electrical and Computer Engineering, Lexington, KY; Liming Yu and Kono Sato, Univ of Kentucky, Dept of Mechanical Engineering, Lexington, KY.

In the past several years, many researchers have attempted to grow aligned carbon nanotube (CNT) arrays with fully controlled parameters on various substrates. Among them, the most encouraging results were obtained by using anodized aluminum oxide (AAO) film as the nano-template to confine CNTs geometry. However, previous results were achieved by using aluminum sheet as the substrate that is not favorable for silicon solid-state circuits. Experiments on CNT array growth from AAO thin film templates on silicon substrates were tried without much success. In this paper, we report, for the first time, highly ordered CNT arrays synthesized with high density and uniformity by a flame method using a porous AAO film as template on silicon wafer. This AAO template was fabricated by using anodization of aluminum film on Si substrate in 0.2M oxalic solution. The CNTs template aligned with vertical structure 1 μm were obtained. Cylindrical constant was deposited at the bottom of the nano-pores in an aqueous solution mixed with cobalt sulfate hydrate, boric acid and acetic acid under AC current. The CNTs were grown on those templates by a flame method using ethylene as the carbon source. Highly-ordered carbon nanotube arrays with high density and uniformity were successfully synthesized by the flame method on silicon substrate. The diameter and length of these carbon nanotubes (CNTs) are controllable with the template structure leading to the shortest nanotubes (500 nm long) ever reported. In addition, the nanotubes were found to be open-tipped and have
strong interactions with the alumina sidewalls. These results show the feasibility of integration between CNT molecular arrays and the silicon microelectronics, which may find application in smart sensor arrays or molecular electronic devices.

Z3.7
Abstract Withdrawn.

Z3.8
EFFECTS OF FE FILM THICKNESS AND AMMONIA ON THE GROWTH BEHAVIOR OF CARBON NANOTUBES GROWN BY THERMAL CHEMICAL VAPOR DEPOSITION. Jung-Inn Sohn, Cheol-Jong Choi, Tae-Young Seong, Seonghoon Lee, Kwangju Institute of Science and Technology (KJIST), Dept of Materials Science and Engineering, Kwangju, KOREA.
Carbon nanotubes are of considerable importance because of their potential technological applications, such as gas reservoirs, battery electrodes, and electronic field emission displays. As a first step, we used this technique to synthesize vertically aligned carbon nanotubes on commercially available low-cost substrates such as silicon. Several growth methods of thermal vapor deposition have been used to synthesize carbon nanotubes. In this work, we investigate the effects of Fe film thickness and ammonia on the growth behavior of carbon nanotubes using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Carbon nanotubes were grown on Fe-deposited Si (001) substrates by thermal CVD. The Fe films were deposited for 20 s - 20 min by pulse-laser deposition. Ammonia was introduced to activate the Fe film prior to the CVD growth of carbon nanotubes. For some samples, the Fe films were used instead, in order to compare with ammonia. SEM results show that the sheet growth characteristics of carbon nanotubes strongly depend on the Fe film deposition time. TEM results show that the CVD growth at 800°C causes the continuous Fe film to be broken down into nanoparticles 5 - 60 nm across the discontinuous islands 100 - 1.1 mm in size. The TEM and SEM results show that the Fe nanoparticles and the amorphous graphene layers are oriented perpendicular to the top surface. Based on X-ray photoelectron spectroscopy and SEM results, possible mechanisms are given to describe the growth mode and the growth behavior of carbon nanotubes.

Z3.9
OBSERVATION OF TITANIUM OXIDE NANOFLAKE-LIKE ARRAYS PREPARED BY ANODIC OXIDATION. Dae-Won Goo, Chang-A, Grimes, Suresh Singh, Zhi Chen, University of Kentucky, Electrical and Computer Engineering Department, Lexington, KY; Wenqiong Hu, Elizabeth C. Dickey, University of Kentucky, Department of Chemical and Materials Engineering, Lexington, KY.
Nano-sized titanium oxide materials are desirable for catalytic and gas sensing applications. In this work, nano-sized titanium oxide structures were achieved through anodization of pure titanium sheets in diluted hydrofluoric aqueous solution. Besides the continuously nano-porous films, nano-flake-like features were observed under certain anodizing conditions. These titanium oxide nanostructures were self-assembled into well-aligned arrays and their diameters were controllable with anodizing voltage. In 1.5% wt HF aqueous solution, typical value of the tube diameter ranged from 20 mm to 60 mm, corresponding to anodizing voltage from 10 V to 20 V. The length of these tubes were limited to about 300 mm and did not increase with the prolonged anodization time. At the bottom of tubes, a domeshaped barrier layer was observed, which was similar to those of anodized aluminum oxide. The SEM images of samples anodized for varying time revealed that the nano-flake-like structures were developing from continuously porous film that were formed during removal of the anodic oxide layer at surface. Some possible growth mechanisms of the nano-flake-like structures are presented.

Z3.10
STRUCTURE OF FRILLED CARBON NANOWIRES SYNTHESIZED BY SULFUR-ASSISTED CHEMICAL VAPOR DEPOSITION. Yeong-Soo Yi, Takashi Mitani, Takashi Sekiguchi, National Institute for Materials Science (NIMS), Nanomaterials Laboratory, Tsukuba, JAPAN; Young-Zum Yang, Hiroshi Akiyama, Hiroshi Horiuchi, NIMS, Advanced Materials Laboratory, Tsukuba, JAPAN; Mikiko N. Grant, University of Tsukuba, Institute of Applied Physics and Center for Tsukuba Advanced Research Alliance, Tsukuba, JAPAN.
Effects of sulfur addition during the growth of carbon nanowires were studied by high-resolution transmission electron microscopy (HRTEM). The carbon nanowires were synthesized by microwave plasma CVD method using mixture of H2S (500ppm) and SiH4 in the gas phase. The HRTEM images revealed that the nanowires grown without H2S were multi-wall carbon nanotubes (MWCNTs). The diameter of these MWCNTs was ranged from 10 to 100 nm. In contrast, the carbon nanowires grown with H2S was not a simple MWCNT; thin lines near the surface of sulfur-assisted grown carbon nanowires were split as a “frill”. The frill structure of the frilled nanowires was found to be thin nanowire or multi layers. It is not clear whether the anomalous, frill-like structure was yielded whether during sulfur-assisted growth process or after the formation of ordal MWCNTs. In either case, we speculate that the chemical effect of sulfur should yield the frill structure. We may expect to modify a MWCNT intentionally into a single-wall CNT by using sulfur.

Z3.11
To build nanotube based nanodevices, controlling the growth of aligned carbon nanotubes will be essential. Our group reported a method for growing aligned nanotube selectively on SiO2 surfaces by thermal chemical vapor deposition (CVD) method from xylene-metallocene mixtures. Here we will describe further studies on the role of size and thickness of patterned oxide structures for the aligned and controlled growth of carbon nanotubes. Patterned SiO2/Si substrates prepared by conventional microfabrication techniques such as lithography and dry & wet etching methods were exposed to xylene-metallocene mixture at 800°C. By defining the size and the thickness of the pattern we could control the orientation of nanotube growth and the degree of nanotube alignment.

Z3.12
CFD ANALYSIS ON A VORTEX ENHANCED CVD REACTOR DESIGN. Kinumori Kawag, Univ of Kentucky, Dept of Mechanical Engineering, Lexington, KY; Rodney Andrews, Univ of Kentucky, Center for Applied Research, Lexington, KY.
To enhance the yield of multi-walled carbon nanotubes (MWCNTs), a vortex enhanced CVD reactor (VECD) design has more advantage over the conventional straight tube CVD with a flat substrate that is currently in operation in the Center for Applied Energy Research at the University of Kentucky. A commercial CFD code was applied to analyze heat and mass transfer processes without chemical reactions in order to compare the old CVD design performance with a new type. First we conducted CFD calculations on three different types of conventional CVD design. We created unstructured grids in the boundary fitted coordinate and tested three different configurations: a horizontally oriented tube with and without a substrate, and a vertically oriented tube with the bottom injection. The injection result in non-uniform flow along the tube, a potential cause of yielding amorphous carbon (impurity for carbon nanotubes). The second design result in a uniform flow pattern along the tube suggesting a better flow pattern than the first type. However, for the purpose of production effectiveness, the vertical orientation is more attractive, so the third design was tested, but no circulation was obtained. VECD is expected to have a longer residence time by an enhanced circulation flow along the tube than the currently available straight tube CVD design. To assess the effect of fluid dynamics without heat transfer on the generation of circulation, a CFD calculation without heat transfer was performed on a vertically oriented tube with the bottom injection. The calculation showed a strong and uniform circulation along the tube with higher mass transfer rate than the conventional CVD. This CFD prediction will be tested against a laboratory scale experiment.

Z3.13
RELIABLY MEASURED SYNTHESIS OF C60@SWNT IN 90% YIELDS. Brian W. Smith, Richard M. Russe, B.C. Satwikumar, Frances Scardino, David T. Louie, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA.
In previous works, we have shown our discovery of C60@SWNT and first describable Arinthe mechanism of filling, which involves the vapor phase transport of C60 molecules to openings in the SWNT's wall. Here, we discuss the high-yield synthesis of C60@SWNT by a new method. Yields are measured by a calibrated weight uptake technique, a methodology that is not subject to the potential pitfalls of other techniques that have been applied. At certain processing conditions, yields exceeding 90% were obtained and correlated to nanotube growth rate. From our data, we determine the parameters that support our growth conditions for obtaining high performance scaffolds for the creation of endohedral SWNT supermolecular assemblies by the vapor phase method.
results pave the way for successful single-tube measurements and for high-yield filling with non-fullerenes.

23.14 CARBON NANOTUBE NETWORK SYNTHESIZED USING MICROWAVE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION. Daling Yang, Qing-Yan Zhang, S.F. Yoon, J.Ahn, Sigun Wang, Nanyang Technological University, Microelectronics Centre, School of Electrical and Electronic Engineering, SINGAPORE.

A new carbon nanotube network is prepared using microwave plasma enhanced chemical vapor deposition under plasma of a mixture of methane, hydrogen and nitrogen at 720°C. The Field Emission Scanning Electron Microscopy images show that the carbon nanotube network is selforganized into needle cylinder, different from the previously reported carbon nanotube ropes or nanofibers. The needle cylinders are about 1 micron in diameter, more than 10 micron in length and composed of hundreds of carbon nanotubes with the diameter from 20 to 100nm. Energy Dispersive X-Ray (EDX) results confirm that the network is carbon in nature, with a small amount of Ni which was used as catalyst. Raman scattering results show G-peak ($1583cm^{-1}$) and D-peak ($1350cm^{-1}$) in the spectra, indicating a graphitic structure. XRD results are found to be consistent with EDX and Raman results. The correlation between the position, intensity of the peak and morphology of carbon nanotube network is also discussed.

23.15 FORMATION OF SINGLE-WALL CARBON NANOHORN SUPPORTED BY METAL PARTICLES USING CO2 LASER VAPORIZATION. Daisuke Kasuga, Department of Material Science and Engineering, Faculty of Science and Technology, Meijo University, Nagoya, Aichi, Japan; Nanotube Project, Japan Science and Technology, c/o NEC, Tsukuba, Ibaraki, JAPAN; Kunimitsu Takehashi, Fumio Koki, Institute of Research and Innovation, Kawasaki, Chiba, JAPAN; Samio Iijima, Department of Material Science and Engineering, Faculty of Science and Technology, Meijo University, Nagoya, Aichi, JAPAN; “Nanotubulated” Project, Japan Science and Technology, c/o NEC, Tsukuba, Ibaraki, JAPAN, NEC Corporation, Tsukuba, Ibaraki, JAPAN.

A single-wall carbon nanohorn (SWNH) is a horn-shaped composed of single-wall graphene sheets with diameters of 2 to 3 nm, and they form a “diamond-like” aggregate with a diameter of about 80 nm [1]. Previous studies have confirmed that SWNHs were heat-resistant in vacuum at up to 1800°C [1], while single-wall carbon nanotubes (SWNTs) collapsed with neighbors in vacuum at 1400 or 1500°C [2]. We recently found that the size and structure of the “diamond-like” SWNH aggregates did not change greatly when they were exposed to 760 torr O2 gas at 550°C. Since SWNHs are stable carbon nanomaterials, they will be useful if they are chemically modified. In this report, we introduce a method of producing SWNHs supported by metal particles, such as Pt, Pd, and Gd. We produced SWNHs supported by metal particles by the CO2 laser vaporization of metal-carbon composite in 760 torr of Ar gas at room temperature. The structures of the obtained materials were studied with transmission electron microscopy (TEM) and Raman spectra. When the platinum-carbon [0.6-0.94 at%] composite was vaporized at 20 kW/m², most of the products were SWNHs supported by platinum particles with diameters of 5 to 10 nm. At the higher laser power density [50 kW/m²], amorphous carbon particles supported by platinum particles with diameters of 5 to 10 nm containing a little quantity of SWNHs with diameters of about 1.2 nm were produced. This work was supported by the US Office of Naval Research (ONR-N00140010762).

References:

23.16 Abstract Withdrawn.

23.17 Abstract Withdrawn.

23.18 Abstract Withdrawn.

23.19 Abstract Withdrawn.

23.20 EFFECT OF CATALYST ON GROWTH BEHAVIOR OF CARBON NANOTUBE SYNTHESIZED BY MICROWAVE HEATING THERMAL CVD PROCESS. Yu-Chen Chang, George C.Tu, Cheng-Pei Kuo, Department of Materials Science and Engineering, National Chiao-Tung University, Hsin-Chu, TAIWAN ROC; Jian-Yi Wang, Materials and Electro-Optics Research Division, Chang-Shan Institute of Science and Technology, Tso-Yuan, TAIWAN ROC; I-Lan Lin, Materials Science Center, National Tsing-Hua University, Hsin-Chu, TAIWAN ROC.

Carbon nanotubes (CNTs) exhibiting good electronic field emission properties have successfully synthesized using a novel chemical vapor deposition process in which the substrates were heated by a susceptor via the absorption of microwave. Morphology of the CNTs coated on silicon substrate varies with the form of catalyst used. The growth behavior is also pronouncedly influenced whenever the plasma was induced in the deposition chamber. Bias applied insitu further improved the synthesis of the aligned CNTs. Thus obtained CNTs own largest number density and exhibit largest emission current density when using sputtered Ni as catalyst. The electron field emission can be turned on at 0.28 V/µm, attaining the current density of 1.3 × 10⁶ A/cm² under 5.5 V/µm applied field, even though the CNTs are randomly oriented. These CNTs possess good enough electronic field emission properties for applications as electronic emitters in field emission display.

23.21 OBSERVATIONAL GROWTH OF CARBON NANOTUBE. Shen Zhu, USRA, NASA/Marshall Space Flight Center, Huntsville, AL; Chiu-Hua Su, S. Lehotay, Microgravity Science and Applications Department, Science Directorate, NASA/Marshall Space Flight Center, Huntsville, AL; J.C. Costaes, USRA, NASA/ Marshall Space Flight Center, Huntsville, AL; Y. Cui; A. Burgner, Center for Photonic Materials, Fisk University, Nashville, TN.

Since the superior properties of multi-wall carbon nanotubes (MWNTs) could improve performances of various devices such as microelectronics and sensors, many efforts have been made in synthesizing high quality multi-wall MWNTs. Most applications require uniform aligned MWNTs. In this presentation, we introduce the growth of MWNTs. By using different catalysts, MWNTs will be reported. Carbon nanotubes are synthesized using thermal chemical vapor deposition. Various temperature and pressure are used to fabricate carbon nanotubes. It is found that the nanotube-diameter distribution mainly depends on the catalyst. The growth temperature with the substrate surface normal either along or against the gravity vector, different growth orientations of MWNTs are observed by scanning electron microscopy although the Raman spectra are similar for samples synthesized at different growth locations. The sizes of these carbon nanotubes in each sample are quite uniform and the length of the tube is up to hundreds of micrometers. These results suggest the gravitation effects in the growth of long and small diameter CNTs.

23.22 INFLUENCE OF THE CATALYST PREPARATION ON CARBON NANOFIBERS SYNTHESIZED VIA CATALYTIC CHEMICAL VAPOUR DEPOSITION. Thomas Schiermann, Marcus Thierle, Hartmut Pröbstle, Jochen Frick, University of Würzburg, Physikalisches Institut, Würzburg, GERMANY; Bernd Schmidt, Grafen Reinach, Bavarian Center for Applied Energy Research (ZAE), Würzburg, GERMANY; Wolfgang Braue, German Aerospace Center (DLR), Materials Research Institute, Cologne, GERMANY.

There is widespread interest in growing carbon nanofibers with defined structure, morphology and a narrow diameter distribution in order to optimize these characteristic features for applications e.g. in the fields of hydrogen storage or battery electrodes. When synthesized via catalytic deposition of carbon-containing gases using transition metal powders or supported metals as catalyst, one of the key parameters for the structure of the nanofibers is the catalyst. Within the framework of this study we investigated effects of the synthesis, different pretreatment processes prior to carbon deposition as well as the preparation (supported / unsupported) of various catalysts (e.g. Ni, Ni/Cu) on the fiber characteristics. The catalysts were characterized by X-ray diffraction methods, electron microscopy, gas sorption, X-ray photoelectron spectroscopy and inductively coupled plasma spectrometry. The carbon deposit was analyzed by scanning and transmission electron microscopy to visualize the catalyst and the carbon nanofiber morphology. The crystallinity, the arrangement of the graphitic planes and the diameter distribution of the nanofibers as well as the catalyst particles embedded in or attached to the fibers were analyzed via X-ray diffraction measurements, Raman spectroscopy, thermogravimetry and high resolution transmission electron microscopy.


Comprehensive imaging and spectroscopy of the plume of material
generated by nanosecond laser vaporization (LV) for single wall carbon nanotube (SWNT) synthesis indicated that SWNT grow by the condensed phase conversion (CPC) of carbon clusters or nanoparticles by metal catalyst nanoparticles (diameters, 20 nm) during the several seconds typically spent by the plume inside the hot oven. Ex situ annealing of soots prepared by time-limited growth of SWNT using these diagnostics recently showed that growth could continue at relatively low temperatures ~1000°C inside the laser vaporization apparatus, supporting the CPC growth model. These results present opportunities for optimizing CPC growth of SWNT both in terms of purity and from the perspective of nanotube and cluster feedstocks (as recently reported for CdS/Ni by Schieltzer et al., Science 2012, 1136 (2001)).

To investigate the effect of nanoparticle density on SWNT yield and growth rates during the annealing period, the pulse width of the laser vaporization was drastically changed to 150 microseconds (~800 500-nm-pulses, figure 1A) and the composite C/Co target. This modification results in a natural consolidation, a tenfold increase in growth rate or the short-pulse synthesis approach. Growth rates (estimated through in situ imaging) and material characteristics (from ex situ TEM, XAS, FEG-SEM, Raman spectroscopy) will be presented. Material collected after incomplete conversion will be tested for continued CPC growth.

Ex situ annealing experiments will also be described using different carbon clusters and nanoparticles as feedstocks to investigate the growth of SWNT by CPC. Rapid thermal annealing is accomplished by CO2 laser irradiation with in situ pyrometry utilized to estimate the sample temperature.

This research was sponsored by the U.S. Department of Energy and the Laboratory-Directed Research and Development Program at ORNL under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

Z3.24 EFFECT OF RF. AND DC-BIAS ON THE GROWTH OF CARBON NANOTUBES USING ELECTRON CYCLOTRON RESONANCE CHEMICAL VAPOR DEPOSITION (ECR-CVD). Y. S. Lee, D. Y. Jeon, Korea Advanced Institute of Science and Technology, Daejeon, KOREA.

Low temperature synthesis of carbon nanotubes (CNTs) is likely required to fabricate electronic devices such as field emitters, transistors, and microelectromechanical systems. In this respect, electron cyclotron resonance chemical vapor deposition (ECR-CVD) is one of promising routes since its plasma zone is apart from the substrate surface so that substrate temperatures are usually kept low during deposition. Moreover ECR-CVD has a high plasma density, generally giving rise to high growth rates of films. We have successfully synthesized vertically aligned CNTs on glass substrates with a methane gas at temperatures as low as 500°C using ECR-CVD. Ni, Co, Fe, and their alloy were used as a catalyst layer. Radio frequency and/or direct current bias voltages was applied to the substrate in order to study the effect of bombardment energy of ions on the growth of CNTs. It was observed by scanning electron microscopy that the morphology of micro pore, total gas pressure, and bias voltages varied the diameters and lengths of CNTs. Active chemical species in a methane gas plasma were identified using optical emission spectrometry and mass spectrometry. Relative ratios and total quantities of active species were varied with microwave power and total gas pressures. However, the RF and/or DC bias made little quantitive effect on the radical species. This is based on the fact that ECR plasma density is much higher than that of RF and/or DC plasma. From this investigation, it was shown that ion bombardment as well as the active species in the plasma also give a great influence on the synthesis of CNTs. In addition, field emission properties of CNTs were also measured.

Z3.25 THERMAL AND MECHANICAL PROPERTIES OF POLY(ETHYLENE OXIDE)-BASED CARBON NANOTUBE COMPOSITES. H. Geng1, H. Shimoda2, L. Fleming1, B. Zheng3, J. Liu4 and O. Zhou5. 1University of North Carolina, Chapel Hill, NC, 2Duke University, Durham, NC.

Poly(ethylene oxide) (PEO) has been investigated for many years as a candidate solid electrolyte material due to its high ionic conductivity in the amorphous state. However, at ambient conditions, PEO is a semi-crystalline material with a crystallization temperature of ~70°C. As a result, PEO has always been considered as a possible route to stabilize the amorphous phase of PEO at room temperature. Carbon nanotubes with dimensions comparable to that of the polymer chain and promoting properties in an attractive filler material. We have fabricated PEO/carbon nanotube composites using both purified and chemically functionalized single-walled carbon nanotubes (SWNTs). Different scanning calorimetry (DSC) and x-ray diffraction results show that their crystallinity decreases with increasing nanotube concentrations. Dynamic mechanical analysis (DMA) results show an improvement of the mechanical properties of PEO by adding nanotubes.

Z3.26 ENHANCED BRIGHTNESS IN MEH-PPV BASED OLEDS USING A CARBON NANOTUBE COMPOSITE AS A CHARGE TRANSPORT LAYER. Jonathan Coleman, Marcus Paulhus, Patrick Fourant and Norton O’Brien, Martin Croke, Werner Blinn, Trinity College Dublin, Dept. of Physics, Dublin, IRELAND.

Organic light emitting diodes have been fabricated, incorporating carbon nanotube based composite as charge injection layers. At moderate nanotube loading levels, charge injection into MEH-PPV was increased by over three orders of magnitude. This was accomplished by a substantial increase in electroluminescent efficiency. This is explained by improved current balance leading to higher singlet exciton yield.

Z3.27 A STUDY OF NYLON-6/CARBON NANOTUBE COMPOSITES. Zhijue Jin, Caiji Xu, Ming Zhang, Ji Liang, Dehui Wu, Tsinghua University, Dept. of Mechanical Engineering, Beijing, CHINA; Bingwei Wei, Reussner Polytechnic Institute, Dept. of Materials Science and Engineering, Troy, NY.

A new technique for fabricating nylon-6/carbon nanotube (PA6/CNT) composites was investigated. Through the use of an improved in situ process, the tensile strength of PA6/CNT composites improved significantly, although the toughness and elongation were compromised. The nucleation of cracks and the breaking of the composites happened not at the interphase but at the wrapping CNTs PA6 layer/PA6 matrix interface.

Keywords: Carbon nanotube, Nylon-6, composite, in-situ Process.

Z3.28 TRANSPORT PROPERTIES AND PERCOLATION IN CARBON NANOTUBES/PMMa COMPOSITES. Jean Michel Benoit, Benoit Corinne, Serge Lechat IEM, Univ. Nancy, FRANCE, Patrick Bernier, GIP 8, Univ. Montpellier; FRANCE; Olivier Chauvet, IEM, Univ. Nancy, FRANCE.

Carbon nanotubes (CNT) possess remarkable physical properties. However, because of their size, they are difficult to handle. Making composites with them gives an alternative way to handle these objects and to make use of their properties at a macroscopic scale. Here, we present a comparative study of the transport properties of PMMA/ CNT nanocomposites thin films with both SWNTs and MWNTs. At room temperature, the conductivity of the composites allows for a pure percolation behavior when increasing the nanotube content. The universal scaling law for random site percolation with a very low percolation threshold (0.07 weight % for SWNTs) is obeyed over two orders of magnitude in CNT content. These composite films may be used as semitransparent and conducting electrodes. At low temperature, SWNTs composites and MWNTs ones behave differently. While MWNTs composites still obey the percolation law, deviations are observed for SWNTs. They are discussed in terms of tube-tube contact and charging energy of the tubes. Very high non linear response to moderate electric fields are also observed in SWNTs composites. The high field conductivity can be orders of magnitude higher than the low field one. It is independent of temperature suggesting tunnelling between metallic tubes. These properties are discussed within the framework of percolation theory and transport in heterogeneous media.

This work is partly supported by the EEC COMELCAN HIPRN-CT-2003-01028 contract.

Z3.29 FABRICATION AND CHARACTERIZATION OF A SERIES OF POLYMER/SINGLE-WALL CARBON NANOTUBE COMPOSITES. Thomas Geometric, Anno K. Burwell, Department of Chemistry and Center for Materials Science, Rochester Institute of Technology, Rochester, NY; Anne C. Dillon, Jeff L. Alleman, Kim M. Jones, Michael J. Heben, National Renewable Energy Laboratory, Golden, CO.

The extraordinary mechanical properties of single wall carbon nanotubes have attracted a great deal of attention for their use in nanocomposite polymer composites. Initial studies have shown the possibility of improved physical properties relative to the traditional carbon fiber-polymer composites. A key important factor is to determine the strength of the nanotube-polymer interface through the evaluation of series of nanotube-polymer materials. This contribution describes ongoing work focused on understanding the nature of the nanotube-polymer matrix interactions. Highly purified (>98%) by
weight) single-walled carbon nanotubes (SWNTs) were obtained through a purification procedure described earlier. A series of polymers including, polyethylene, polypropylene, polycrylonitrile, poly(vinyl butyral), poly(methacrylate), poly(vinyl pyridine), polytetrafluoroethylene, polyamide and Nafion were investigated. The nanotubes were incorporated into the polymer solution through a series of homogenization and folding techniques for a doping range from 0.05% to 20% by weight nanotubes. Ultrasonication was not used in order to minimize damage to the nanotube materials. The resultant solutions and solution cast thin-films were characterized by optical absorption microscopy, electron microscopy, Raman spectroscopy, thermal analysis (DSC, DTA), electrochemical and resistivity techniques. Specifically, we have achieved dissolution of carbon nanotubes in several polymers to such an extent that the homogeneous solutions survived ultracentrifugation without any phase separation of the nanotubes. The polymeric properties that lead to these strong interactions and the unique physical properties of the composites will be discussed.


Polymer-single wall carbon nanotube (SWNT) composite films were prepared and characterized as part of an effort to develop polymer materials with improved combinations of properties for potential use on future spacecraft. A new process for synthesizing large quantities of ultra-pure, ultra-lightweight materials that possess specific and unique combinations of properties such as radiation and atomic oxygen resistance, low soh absorptivity, high thermal emittance, electrical conductivity, ability to form a sheet, and good mechanical properties. The objective of this work is to incorporate sufficient electrical conductivity into space durable polymides to mitigate static charge buildup. The challenge is to obtain the level of conductivity (10^-6 S/cm) without degrading other properties of importance, particularly solar absorptivity. Several different approaches were attempted to full disseminate the SWNTs into the polymer matrix. These included high shear mixing, sonication, and synthesizing the polymers in the presence of dispersed SWNTs. In some cases, acceptable levels of conductivity were obtained at loading levels less than one weight percent SWNTs. Characterization of the nanocomposite films and the effect of SWNT concentration and dispersion on the conductivity, solar absorptivity, and mechanical properties will be presented.

Z3.31 DISPERSION AND ALIGNMENT OF CARBON NANOTUBES IN THERMOPLASTIC POLYMERS. Mike Sennett, J.B. Wright, E.A. Welsh, US Army Soldier and Biological Chemical Command, Natick Soldier Center, Materials Science Team, Natick, MA; W. Li, J.G. Wen, Z.F. Ren, Boston College, Dept of Physics, Chestnut Hill, MA.

Dispersion and alignment of carbon nanotubes (CNT) in thermoplastic polymers such as polycarbonate (PC) have been studied. Dispersion and alignment were accomplished using an extruder and orientation was carried out using a fiber spinning apparatus. The effects of mixing time and fiber draw rates on dispersion and alignment were investigated. Shorter residence times in the extruder were required to produce uniform dispersion. Excellent alignment of CNT in nanocomposite films was obtained when the fiber draw rate was greater than 70 meter/min. The ability to closely control the dispersion and alignment of carbon nanotubes in polymers is expected to lead to the development of nanocomposites with desirable electronic and structural properties.

Z3.32 SCANNING PROBE AND HIGH RESOLUTION ELECTRON MICROSCOPY STUDY OF SINGLE WALL CARBON NANOTUBE POLYMER COMPOSITES. Peter T. Lilecke, Chell Park*, Roy Galias*, **, and Emily J. Siodu, Advanced Materials and Processing Branch, NASA Langley Research Center, CASE, **Lockheed Martin, Hampton, VA.

Single wall carbon nanotube (SWNT) reinforced polymer composites are of great interest in aerospace applications because of their potential for tremendous property improvements over conventional materials. The production of composites with optimal properties requires control of the SWNT dispersion within the polymer matrix. Evaluation of processing parameters relies on effective high-resolution characterization methods. This study correlates the results of both scanning probe microscopy (SPM) and high resolution transmission electron microscopy (HREM) imaging of SWNT polymer composites. SPM methods used include magnetic force microscopy (MFM), nanindentation and force spectroscopy. HREM study was hindered by the weak contrast of the SWNT within the composite, and two methods were used for contrast enhancement with some success. Image mixing, utilizing several polymer matrixes and the SWNTs were used to enhance the periodicity contrast of the SWNT against the polymer matrix. Electron energy loss (EELS) spectra for isolated SWNTs, polyamide and the SWNT-polyamide composite are compared. The relative usefulness of electron energy loss measurements (EELS) information and ionization edge peaks is shown for energy filtered mapping of SWNT distributions within the polymer matrix.

Z3.33 SYNTHESIS AND CHARACTERIZATION OF SINGLE-WALL CARBON NANOTUBE/α-C TIN FILM COMPOSITES. C.H. Schetterling, D.B. Geoghegan, P.F. Brit, Oak Ridge National Laboratory, Oak Ridge, TN; Materials Science and Engineering, Univ. of Tennessee, Knoxville, TN.

Multifunctional composites which combine the exceptional electronic, mechanical or thermal properties of single-wall carbon nanotubes (SWNT) with those of a matrix material are envisioned for a wide range of applications. Here we report the first synthesis of composites which utilize ultrahard, transparent, amorphous diamond thin films as matrices to encapsulate conducting SWNT masses. This film is intended to provide a transparent, wear-resistant coating to shield the SWNT against mechanical deformation and adsorption of common ambient gases or liquids which have been observed to strongly modify their electronic properties.

SWNT were synthesized by laser evaporation and chemically purified to > 95 wt. % SWNT as measured by TGA analysis. A diamond precursor suspension was then spray coated onto Si, quartz, and other substrates to form films of varying areal densities. Pulsed laser deposition (PLD) of tetragonally-crystallized amorphous carbon was then performed in vacuum using a pyrolytic graphite target irradiated at 10KeV, generating a plasma containing carbon ions with kinetic energies up to >10000 eV. The interactions of these high energy ions with the SWNT are of fundamental interest for the general use of PLD to form SWNT thin film composites. The resistivity of the mass was measured in situ during film deposition, while ex situ measurements before and after deposition included L-V measurements, along with FIESEM, TEM and Raman scattering analyses. Resonant Raman spectra from the SWNT and visible and near-infrared absorption spectra from these films show that a large fraction of the SWNT survive the energetic deposition process, with the characteristic tangential and breathing modes remaining unchanged in shape and position but decreased in magnitude. An interesting disorder band was observed, as expected. Preliminary results indicate that amorphous diamond thin films can be used as protective matrices for multifunctional SWNT composites.

This research was sponsored by the Advanced Materials and Processing Branch at NASA-LaRC, the Nanotechnology CDF at NASA-MSFC, and the U.S. Department of Energy under contract DE-AC05-8906R2725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

Z3.34 CARBON-NANOTUBE-BINDING PEPTIDES: BUILDING BLOCKS FOR SLUSHY NANOSTRUCTURES. R. Smith, N. Sesti, D.A. Waters, Univ. of Central Florida, Orlando, FL; P.A. Willis, R.E. Smalley, Rice Univ, Houston, TX.

We developed oligopeptides, short sequences of amino acids, which show binding activity to carbon nanotubes (CNTs). A random library of ~10^10 peptides, expressed via phage display, was exposed to single-wall CNTs in multiple rounds of biopanning. At each round of the process, phage DNA was extracted and sequenced to determine the peptide sequence. Binding was assessed by imaging phage-CNT complexes with an atomic force microscope. The resulting peptides are general tools for manipulation and assembly of CNTs. Applications to purification, separation, lithography, and nanomechanical devices will be discussed. The authors acknowledge the generous assistance of Dr. Debopam Chakraborty and his students for providing advice and access to equipment.

This work was funded by the Office of Naval Research and the UCF Office of Research.

Z3.35 METAL-OrgANIC SELF-ASSEMBLY OF FUNCTIONALIZED CARBON NANOTUBES IN WATERS: FOREST-LIKE ASSEMBLIES. Fotis Papadimitrakopoulos, Debjit Chattopadhyay, Ishbel Galeski, Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT.

Substrate independent, normal organization of single wall carbon nanotubes (SWNTs) holds significant promise for nanoscale devices.
Herein we demonstrate that DMF dispersed SWNTs can be successfully organized in dense (up to 1.1 g/cm³), highly oriented regular arrays of substrates by a simple self-assembly process both in monolayer and multilayer forms. This unique self-assembly is based on the acid-base interactions of the carboxyl terminated nanotubes with the Fe(III) decorated surface. Tapping mode atomic force microscopy (AFM) clearly shows that the SWNTs can be directed perpendicular to the surface. Raman and spectroscopic ellipsometry investigation on these assemblies corroborate the orthogonal orientation observed by AFM. Thickness measurements on these films measured monolayer thickness (i.e. nanotube length) of 37.7 nm. Quartz Crystal Microbalance (QCM) along with ellipsometry studies provide additional insight into the density of these films, yielding densities up to 1.1 g/cm³. The fast adsorption and perpendicularly alignment of SWNTs can open up a wide scope of possible applications ranging from optoelectronics to biological sensors.

SESSION 24: NANOTUBE-POLYMER COMPOSITES

Chair: Masako Yoshikawa and Serge R. Leblanc
Tuesday Morning, November 27, 2001
Back Bay A (Sheraton)

8:30 AM *24.1* ISSUES IN THE PROCESSING AND PROPERTIES OF MULTI-WALLED CARBON NANOtube-POLYMER COMPOSITES

Paul E. Etir, P.M. Ajayan, Rensselaer Polytechnic Institute, Troy, NY.

One of the biggest technical challenges in taking advantage of the interesting properties of carbon nanotubes in polymer nanocomposites is controlling the degree of dispersion and removing unwanted carbonaceous material. We have made considerable progress in understanding and optimizing the purification of resin-dispersion based multi-walled carbon nanotubes (MWNT) and in optimizing the degree of interaction between the polymer matrix and the MWNT. For example, we have achieved transparent dispersions of MWNT in aromatic monomers. This is leading to an ability to control the mechanical properties of MWNT/polymer nanocomposites. This talk will highlight our recent advances in the processing of composites and we will report on the wear resistance as well as tensile and compression properties of MWNT/polymer nanocomposites.

9:00 AM *24.2* PROCESSING AND PROPERTIES OF POLYMER NANOTUBE MATRICES

Rodney Andrews, Terry Rantanen, Univ. of Kentucky, Center for Applied Energy Research, Lexington, IA; John Anthony, Robert G. Bergoth, Chad Landis, Mark S. Meier, Univ of Kentucky, Dept of Chemistry, Lexington, KY.

Harnessing the unique physical properties of MWNTs in materials applications is yet to be fully realized. In recent work at CAER, MWNTs have been dispersed in polymers and pitch matrices by using ultrasonic to disperse MWNT into solutions. However, this approach, although providing valuable information on methods for realizing the remarkable properties of the MWNT, is not readily translatable to industrial practice. A more practical method of producing MWNT composites is by shear mixing followed by extrusion or injection molding. The dispersion of nanotubes into polymers and pitch matrices utilizing traditional polymer processing technologies will be discussed. Sufficient dispersion is found to be the key in realizing the potential of these unique nanomaterials. The effect of composite form, nanotube alignment, and functionalization of the nanotube surface for improved adhesion will be discussed in relation to the effect on composite properties.

9:30 AM *24.3* CONDUCTING POLYMER CARBON NANOtube COMPOSITES

Gordon Wallace, My Takeh, Joseph Baran, Geoffrey Spinks, Univ. of Wollongong, Intelligent Polymer Research Institute, Wollongong, NSW, AUSTRALIA; Mei Gao, Lining Dai, CSIRO, Division of Molecular Science, Clayton South, VIC, AUSTRALIA.

Inherently conducting polymers (ICPs) are dynamic structures finding widespread use as sensors, molecular separation systems, electromechanical actuators and energy conversion storage systems. The practical use of many of these systems is limited by either weak mechanical properties or inadequate electronic conductivity. The fascinating electronic and mechanical properties of carbon nanotubes (CNTs) have been the subject of many recent investigations and we now propose to combine these materials with ICPs to produce a range of new composite structures. It is envisaged that the properties of these structures will be such that the current limitations of ICPs will be alleviated. A number of approaches are under investigation. These include: the use of dispersed carbon nanotubes as dopants. CNTs can be dispersed in aqueous solution using anionic dispersants. The 'wet' tubes may then be incorporated into a polymeric matrix during electrospinning. Electrodeposition of ICPs or CNT mats. CNT mats may be prepared using simple filtration approaches. The mats can then be used as an electrode for deposition of ICPs. Use of soluble conducting polymers. The water soluble sulfonated polyaniline has proven to be an effective dopant for CNTs. Formation of composite CNT mats after filtration is possible. Each of these approaches as well as our preliminary attempts to chemically derivatize CNTs to compatibilize the composites will be discussed. The electrochemical and mechanical properties of these new structures have been investigated.

10:30 AM *24.4* ALIGNMENT AND DISPERSION OF SINGLE-WALL CARBON NANOtube IN POLYMER COMPOSITES


Individual single-wall carbon nanotubes (SWNTs) have demonstrated superior mechanical, thermal and electrical properties relative to carbon fibers. Thus, an obvious direction is to produce nanotube-polymer composites in an attempt to harness these extraordinary properties. We have produced SWNT-polymer composites using melt mixing methods and a variety of processing conditions (temperature, time, torque). Subsequently, some of these composites have been subjected to melt extrusion to form SWNT-polymer composite fibers. Our early results with SWNT-poly(methyl methacrylate) composite fibers show improved mechanical properties. The elastic modulus of these fibers increases with draw ratio and the weight fraction of SWNT. More importantly, the extensional flow of melt fiber spinning was sufficient to align the SWNT within the polymer matrix. According to polarized Raman spectroscopy, the mosaic distribution of the fiber axis relative to the fiber axis can be below the mosaic fiber limit of the experiment. While this outstanding SWNT alignment might be an asset for mechanical properties, the alignment of one-dimensional conductors in these composites could reduce electrical conductivity. Our current efforts focus on processing methods to maximize the dispersion of SWNT within a variety of thermoplastics.

11:00 AM *24.5* OPTICAL AND ELECTRO-OPTIC PROPERTIES OF CARBON NANOtube MATRIX COMPOSITES

David L. Carroll, Richard Czerv, Scott Webster, Dept. of Physics, Clemson Univ., Clemson, SC; Nirupama Chundrani, Pulolli M. Ajayan, Dept. of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY.

Optically active composites made from single wall carbon nanotubes (SWNTs) and a laser dye (Rhodamine B, Coumarin 40) or conjugated polymer (MEH-PPV, PFO), containing matrix have been used to study the optical response of isolated nanotubes. Strong modifications to the photoluminescence behavior of dyes and photo-luminescence of conjugated polymers are made as a function of nanotube length and loading. Specifically, enhanced luminescence yields and shifts in emission frequencies are quite pronounced in some cases. Further, extreme photo-sensitivity in electrical transport noise of the conjugated polymer - nanotube composites has been observed. A simple model of dipole coupling between the emissive species and the nanotubes can explain some, but not all of the observed phenomena. This suggests that new-field interactions within the matrix may also play a role in the behavior of "new-type" emission of light. These results will be discussed in terms of several unique applications of the nanotube composites including: optical switching, nonlinear optical materials, organic photovoltaics, and organic light emitting diodes.

11:30 AM *24.6* PROCESSING AND MONITORING OF SINGLE WALL CARBON NANOtube COMPOSITES

Brad Files, NASA Johnson Space Center, Houston, TX; Oguz Gorelik, Pavel Nikolaev, and Sirvand Arepalli, GBTech/Lockheed Martin, Houston, TX; Victor Hudr, Institute for Space Systems Operations and Test Center for Superconductivity, University of Houston, Houston, TX.

Use of the extraordinary mechanical properties of single wall nanotubes presents opportunities for designing new materials to greatly reduce the weight of structural materials that can enable new space vehicles. Various processing methods of nanotube polymer composites show a variety of results depending on the techniques used. Characterization methods such as Raman spectroscopy and dynamic mechanical analysis show that certain molding techniques and processing routes can produce samples with wide-ranging mechanical properties. Measurements show that flaws in most specimens drive properties, since processing of these materials is difficult. Composite production methods to be described include casting, injection molding, compression molding, and lamination. A number of mixing methods
will be discussed, including both manual and mechanical means. Data from mechanical testing will be correlated with various techniques to show those which have proven to be most reliable.

11:45 AM Z4.2

Experimental and theoretical results suggest that carbon nanotubes (CNT) and carbon nanofibres (CNF) hold promise as reinforcement materials for novel polymer nanocomposites. We have investigated a range of composite systems using nanotubes and nanofibres of different structure and diameter in a number of representative thermoplastic matrices, including commodity and high performance resins. We have particularly examined the influence of the nanocarbons on the resulting polymer morphologies with regard to crystallinity in the vicinity of the fillers. Model thin-film nanocomposites have been examined by laser Raman spectroscopy during in-situ microscopic deformation with regard to a shift of the characteristic Raman peak, which indicates an effective load transfer from the matrix to the filler. We have achieved a high degree of dispersion in all matrices, using an intensive shear mixing protocol in conventional thermoplastic processing equipment, and have fabricated macroscopic standard test samples by injection moulding. The degree of dispersion is directly linked to the degree of the dielectric response. As with conventional composites, we have found that the critical factors influencing composite performance are the structural quality of the nanotube and the nature of the filler dispersion.

SESSION 25: NANO TUBES FOR FIELD EMISSION
Chair: Gordon G. Wallace and Karen I. Winney
Tuesday Afternoon, November 27, 2001
Back Bay A (Sheraton)

1:30 P.M. Z5.1
RECENT DEVELOPMENT'S OF CARBON NANOTUBE FIELD EMISSION DISPLAYS. J.M. Kim, FED Team, CRD, Samsung SDA and Samsung Advanced Institute of Technology, Suwon, KOREA.

Carbon nanotube emitters, prepared by screen printing, have demonstrated a great potential towards low-cost, large area field emission displays. Carbon nanotube paste, essential to the screen printing technology, was prepared to exhibit low threshold electric fields as well as emission uniformity over a large area. Two different types of triode structures, normal gate and undercut, have been investigated, leading us to the optimal structure design. These carbon nanotube FEDs demonstrated color separation and high brightness over 3000 fcd/m2 at an video-speed operation of moving images. Our recent developments will be presented in detail.

2:00 P.M. Z6.2
FIELD EMISSION OF CARBON NANOTUBES WITH DIFFERENT LENGTHS. Yan Chen, Jihok Park, Vipal Patel, Nalini Kumar and Bawan Singh, UHV Technologies, Inc., Mount Laurel, NJ.

Field emission data of well-aligned carbon nanotubes with different lengths have been obtained. The aligned carbon nanotubes were synthesized by plasma assisted hot filament chemical vapor deposition using a gas mixture of nitrogen and methane. The filed emission of the carbon nanotube with the length of 500nm, 1µm, 5µm and 10µm have been measured. The lengths of the nanotubes were controlled by growth time. The results indicate that the emission capability is enhanced with the increase of the length. A theoretical model has been established to explain the experiment results.

2:15 P.M. Z6.3
CORRELATIONS OF THE MICROSTRUCTURES OF THE CARBON NANOTUBES AND THEIR FIELD EMISSION PROPERTIES. Jin Joo, Dave Taggle, Lifeng Dong, Sean Foxley, Portland State Univ, Dept of Physics, Portland, OR.

Carbon nanotubes have drawn much attention as electron field emission sources because of their unique geometry and their remarkable electronic properties. In particular the emission from carbon nanotubes at low applied electric fields has been demonstrated by a number of research groups. However, the field emission behavior reported for nanotubes varies widely, and the proposed emission mechanisms are, therefore, quite different. These variations may be attributed differences in the nanotube content of measured samples.

For instance, some samples contain both single-walled and multi-walled nanotubes. Some nanotubes are well aligned while some are randomly oriented. The uniformity of the nanotubes such as the diameter distribution and the purity of the nanotubes are also different from sample to sample. The work reported here aimed at understanding the emission mechanisms of carbon nanotubes by systematic study of the correlation between the microstructures of different carbon nanotubes and their related field emission properties. In this study, the samples of single-walled and multi-walled carbon nanotubes with controlled diameters and aligned orientations are prepared by a chemical vapor deposition method. The field emission properties such as the field emission patterns and the LV characteristics of each sample are measured. The effect of preparation conditions, such as the type of catalyst, the different hydrogen flow, reaction temperatures, and reaction duration on the formation of controlled geometric structures of carbon nanotubes will be discussed. The characteristics of the field emission behavior of each sample with respect to the microstructural features of nanotubes will be analyzed.

3:30 PM Z25.5

Previous studies have indicated that carbon nanotube field emitters can generate large current densities over long periods of time without decay. This ability makes carbon nanotube field emitters ideally suited for application in vacuum microelectronic devices which require current densities in excess of 1 A/cm² such as microwave power amplifiers. Here, we will present our results on designing, fabricating, and testing microtriodes which utilize carbon nanotube cold cathodes. To date, we have observed sustainable current densities in excess of 8 A/cm² and we have tested a microtriode with a DC power gain of 18 dB. We will compare and contrast the performance of this device against other thermionic and field emission triodes.

3:45 PM Z25.6

Carbon nanotubes have attractive electron field emission properties compared to the conventional electron emissive materials such as diamond. They have low threshold fields for emission and are relatively stable at high current densities. Motivated by potential applications in vacuum microelectronic devices, the electron field emission properties of different carbon nanotube materials have been studied in considerable detail in the last few years. In this talk we present results on incorporation of carbon nanotubes into diode and triode type cold-cathode structures. The performances of these cold cathodes will be compared and discussed. In addition, we will present some recent results obtained from carbon nanotube based vacuum microelectronic devices. This work is supported by an ONR MURI program, Agere Systems, and Applied Nanotechnologies, Inc.

4:45 PM Z25.7
THE ROLE OF ADSORBATES ON THE FIELD EMISSION PROPERTIES OF SINGLE-WALLED CARBON NANOTUBES. Raman Cologn, Rascal Schlesser, Zhikai Sitar, Dept of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

Two field-emission states of single-walled carbon nanotubes were identified according to their respective emission current levels. The state yielding increased emission current was attributed to the presence of adsorbates on the nanotubes as confirmed by electron emission measurements at different background pressures. Application
of high electric fields induced large emission currents and a transition between the two states. During this transition, a current drop to 1/10 of the original value was observed. Under a constant applied electric field, the current took around 1000 s to recover its original level as a background pressure of 10−10 Torr, while it took half that time at 10−6 Torr. For the high current state, field-emitted electron beams emitted from sources located 1 eV below the Fermi level, as was determined by field-emission energy distribution measurements. This suggested that the adsorbate film has a field-emission current density of 300 µA/mm², which is very close to the value measured by other workers. The adsorbed molecules can be efficiently emitted from the cathode surface due to the high electric field strength. This adsorption/desorption process is completely reversible.

4:15 PM 25.8
A STUDY OF FIELD EMISSION PROPERTIES OF POLAR AND NON-POLAR MOLECULE DOPED CARBON NANOTUBES
Youngil Song, Brian C. Unger, Jeewoo Choi, Louisiana State University, Center for Advanced Microstructures and Devices, Baton Rouge, LA; Young-Chul Choi, Samsung SDI, Corporate R&D Center, KOREA; Seung-Chul Lim, Jeonbuk National University, Semiconductor Physics Research Center, KOREA, Young Hee Lee, Sungkyunkwan University, Dept. of Physics, KOREA.

We have studied field emission properties of vertically aligned, multi-walled carbon nanotube films and randomly oriented single-walled carbon nanotube films by exposing both samples to polar (nitrogen dioxide) and non-polar (nitrogen oxide) molecules. Because it is attributed that doping with nitrogen dioxide (polar) and nitrogen oxide (non-polar) induces the electronic and physical properties of these carbon nanotubes, the turn-on voltage and emission current density were found to depend on the polarity of the doped molecules and the amount of gas exposed. Specifically, in the case when the carbon nanotube films were doped with the polar nitrogen dioxide, a turn-on voltage and emission current density were observed. Thus, the polarity of the adsorbate plays an important role in the field emission properties of single-walled and multi-walled carbon nanotubes.

4:30 PM 25.9

PECVD is an extremely versatile technique for directly growing multiwalled carbon nanotubes onto various substrates. We will demonstrate the deposition of vertically aligned nanotube arrays, 'spaghetti' nanotubes, sparsely or densely packed nanotube forests, and precisely patterned arrays of single nanotubes. The high aspect ratio nanotubes (~30 nm in diameter and 5 microns long) produced are metallic in nature and direct contact electrical measurements reveal that each nanotube has a current density capacity of ~1 million amps per square centimetre, making them excellent candidates as field emission sources. We examined the field emission characteristics of dense nanotube forests [aligned and non-aligned] as well as single nanotube arrays and found that the single nanotube array exhibited significantly lower turn-on fields and higher emission currents. This is due to electric field shielding from adjacent nanotubes in the dense nanotube array. The maximum macroscopic field emission current achieved is also ~10 A per square centimetre and we believe this is limited by the substrate and the actual number of nanotubes which are emitting. We thus fabricated a uniform array of single nanotubes to overcome these issues and will present the field emission characteristics of this. The fabrication of a grid of microscopic field emission cathode utilising nanotubes will also be presented.

4:45 PM 25.10
Abstract withdrawn.

SESSION 26. POSTER SESSION
CHARACTERIZATION, FIELD EMISSION AND ELECTRONIC DEVICES
Tuesday Evening, November 27, 2001
8:00 PM
Exhibition Hall D (Hynes)

26.1 FIELD EMISSION OF CARBON NANOTUBES ON GLASS SUBSTRATE USING THERMAL, CHEMICAL VAPOR DEPOSITION. C.-W. Sec, J.H. Park, B.D. Min, J.H. Han, Iijin Nanotech Co., Ltd, Nano Technology R&D Center, Seoul, S. KOREA.

Field emitters for flat-panel displays and vacuum microelectronic devices are one of the most promising applications of carbon nanotubes (CNTs). For the application of the CNTs to the field emitters sealed by a glass-film glass, it is practically important to lower the growth temperature at least 550 °C. We will report here the field emission characteristics of CNTs cathode on the glass substrate, which are prepared in the two-stage heating system by the chemical vapor deposition (CVD) method. A Ti film with a thickness of 400 nm is deposited on the glass substrate using the DC sputtering system. Afterwards, catalyst Ni film with a thickness of 30 nm was deposited on the Ti/glass substrate. C6H6 gas was pre-heated in the first zone of the reactor at 800 °C and then brought into the applied CVD chamber at 500°C for the growth of CNTs on the Ni/Ti/glass substrate. The diameters of the CNTs are in the range of 40–60 nm, while their length can be as long as 10 µm. Field emission measurements have been made on the CNTs cathode diode-type device at room temperature and in a vacuum chamber below 10−6 Torr. The distance between the CNTs cathode and anode is 600 µm, which is kept through an insulating spacer. The dimension of field emission area is 1.5 mm × 1.5 mm. The turn-on electric field was 2.9 V/µm as an emission current of 0.1 µA/cm² and the uniform emission current of 1.2 mA/cm² are measured at 5.0 V/µm. The present results showed that the CNTs have the excellent performance as field emitters and issues in actual display devices since 0.1 mA/cm² can produce enough brightness (>1000 cd/m²) under practical operating conditions.


Carbon nanotubes have been shown to have attractive electron field emission properties for potential industrial applications. Compared with the conventional electron emission materials, they have a low threshold electrical field for emission and are capable of emitting high currents. Yet their realization in actual devices has been held back due to difficulties in processing issues such as low emission stability. Here we show that electrophoretic deposition technique can be utilized to deposit pre-form carbon nanotubes on various surfaces and form adhesive films. The results show that these films are more stable at high emission current densities than the freestanding single-wall carbon nanotube membranes. The effects of the processing conditions on the electron field emission properties will be discussed.

26.3 WORK FUNCTION AT THE TIPS OF MULTIWALLED CARBON NANOTUBES Ruiqiu Gao, Nati Natural Sci Foundation and Univ of Sci and Tech, Beijing, Beijing, CHINA; Z.W. Pan and Zhong L. Wang, Cnr for Nanoscience and Nanotechnology, School of MSEE, Georgia Inst of Tech, Atlanta, GA.

The unique geometrical structure of carbon nanotubes suggests that they are likely to be an ideal high-field electrode material for an applied surface. Indeed, numerous field emission measurements show that the carbon nanotubes exhibit superior field emission performance with required field current much lower than those of many other field emitters. For carbon nanotubes, most of the electrons emitted from the tips of the tubes, and it is the local work function that matters to the properties of the tube field emission. Since the lack of suitable experimental methods to measure the work function of carbon nanotubes, the value of work function of carbon nanotubes used in the literatures is mainly from the well-studied carbon or graphite. Thus, it is necessary to experimentally measure the work function of carbon nanotubes. We present experimental measurements of tip work function of individual carbon nanotubes. The experiment was done by a novel in-situ transmission electron microscopy technique [1,2]. Our results indicate that the tip work function show no significant dependence on the diameter of the nanotubes in the range of 14-55 nm (95% of the nanotubes) have work function of 4.64-6.5 V at the tips, which is 0.5-0.8 V lower than that of carbon. A small fraction of the nanotubes (~25%) have a work function of ~5.6 V, about 0.6 V higher than that of carbon. This discrepancy is suggested due to the metallic and semiconductive characteristics of the tubes.

[3] The research was supported by National Natural Science Foundation of China and the US NSF.

26.4 ANTI-Localization CAUSED BY Slight Doping OF HEAVY IMPURITIES INTO ONE END OF CARBON NANOTUBES AND A C G MOS LIKE PHASE-INTERFERENCE
Influence of impurity-doping into carbon nanotubes is currently of great interest, particularly in single walled carbon nanotubes and also fullerene. In contrast, characteristics of multi-walled carbon nanotubes (MWCNTs) have been understood only by phase-interference effects of electron waves. None reported on the influence of impurity-doping on such effects in MWCNTs. In this presentation, we report for the first time on anti-localization (AL) caused by slight impurities in a few nanotubes in only one end of MWCNTs and propose a novel phase-interference transistor like C-MOS, based on this effect. We slightly dope impurity-atoms of electrode-materials into the top end of MWCNTs, standing in nanopores of nanocarbon materials [1]. Doping the light-electrode materials (Carbon and Aluminum) lead to two-dimensional weak localization [WL] in Alkhalil-Arons-Vipin [AAS] calculation, consistent with past reports of MWCNTs [2]. In contrast, we find doping of heavy-element materials (Gold and Platinum) at the volume-ratio of only about 0.5% drastically change this WL to AL [3]. Using revised Alkhalil theory, it is confirmed that spin-orbital interaction in the small-doping-region causes spin-flipping of electrons and introduces these electrons into the bulk of MWCNTs, leading to AL. We also find that this phenomenon is observable only when electrons are injected into the doping region. This turns out that such a small-doping-region acts the important role for polarized injection of spin-flipped-electrons into the bulk of MWCNTs. Series connection of these two types MWCNTs (i.e., with WL and AL) will promise quantum-wave transistor or controllable by magnetic field, like CMOS transistors in semiconductor logic devices, because they exhibit opposite spin in current-change to magnetic field applied (like P and N type-transistors applied a gate voltage).

Z6.5 FABRICATION OF NANO TRANSISTOR BY SELECTIVELY GROWN CARBON NANOTUBE, Won Bong Choi, Jee Uk Chu, Kwang Seok Jeong, Eun Ju Bae, In Kyung Yoo, U-tam, MD Lab, Samsung Advanced Institute of Technology, SAWON, Korea; Jeong Kim, Jeong-O Lee, Department of Physics, Chonbuk National University.

Carbon nanotube has been proposed as an ideal quantum wire for nanoelectronics. Recent progress in carbon nanotube quantum wire has hinted at the achievement of nanoelectronics given the integration technique is supported. However, neither selective growth of carbon nanotubes nor device integration has been achieved. Here we demonstrate a novel type of carbon nanotube transistor, which would be suitable for large-scale integration. We fabricated highly ordered carbon nanotubes, which are selectively grown and narrow in diameter range. Each electrode is formed on a vertically-carbon nanotube attached to a source and drain electrodes and a gate electrode, which is electrostatically switchable. The metal/metal interfaces are modified by annealing and controlled by TEM and L-V characteristics. In this presentation, next-generation switching mechanism of the carbon nanotube transistor will be explained based on the experimental result.

Z6.6 MULTIWALLED CARBON NANOTUBES GROWTH BY CATALYTIC PYROLYSIS IN NANO TEMPLATE AND ITS APPLICATION TO A FIELD EMITTER, Soo-Hyun Jeong, Ok-Joo Lee, Sun-Kyu Hwang, Seo-Kim Hong, Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, KOREA; Kwang-Young Kim, Nam-Seok Kang, LG Electronics Inc., Seoul, KOREA.

The growth of carbon nanotubes (CNTs) in micrometer oxide (AOO) template and their application to a field emitter are described. AOO templates were fabricated by ion milling bulk aluminum and sputter-thin Al film on Si substrates. After Co catalyst had been electrochemically deposited into the bottom of the pores in AOO template, CNTs were grown by catalytic chemical vapor deposition of C2H2 or CO. Depending on the reaction conditions, CNTs grew up to several micrometers long and 100-200 nm in diameter. The CNTs were contacted by electron microscopy, scanning electron microscopy, transmission electron microscopy, etc. The catalyst films with different compositions were observed under an electron microscope. The growth of CNTs strongly depended on the size of the pores in AOO template and the growth conditions. The growth of CNTs caused by C2H2 pyrolysis, the growth of CNTs in a AOO template is significantly influenced by the presence of H2. In all cases, CNTs growth on Co catalyst was competitive reaction with carbon deposition on the AAO template itself. The electron field emission measurements of the samples resulted in the field emission of 1.4x2 V/nm and the field enhancement factor of 2456±5209. The observation of high field enhancement factors is explained in terms of low field screening effect.

Z6.7 SINGLE WALL CARBON NANOTUBE ELECTRON EMITTERS PRODUCED BY ELECTROPHORESIS, E.D. Obrusnov, A.S. Puzhkov, S.V. Terekhov, A.V. Ovodov, S.M. Pimenov, V.I. Konov, National Scientific Center of RAS, RUSSIA; T.A. Skoblikovitch, S.R. Ivanova, General Physics Inst., RAS, Moscow, RUSSIA; A.P. Volkov, A.N. Obrusnov, Physics Department of Moscow State University, RUSSIA.

Single-wall carbon nanotubes (SWNT) find one of the most promising technological applications in a vacuum electronics: the nanotube films could serve as cathodes for new light sources and flat panel displays. Nevertheless the main problem is to find a process, which will allow fabrication of a stable and homogeneous nanotube film. In our work a liquid electrophoresis process has been used for this purpose. SWNT were synthesized in arc. Ni catalyst was used. The raw material was enriched with the tubes via a three-step chemical purification: boiling in HNO3, rinsing and annealing at 550°C in an oxygen-containing atmosphere. As a result the nanotube content has increased from 15 to 70 weight %. Raman and HRETEM techniques were used for the material diagnostics. An electrophoretic deposition of the nanotube films has been performed in an ethanol solution of NaN3. An optimization of the process parameters has allowed to deposit homogeneous thin SWNT films from different substrates (silicon, steel, nickel, metalized glass). The emission characteristics of the SWNT films have been measured. The emission threshold appeared to be quite low ~ 0.1 V/µm. The current was about 5 mA/cm2. The distribution of the emission centers and its temporal evolution (almost negligible) were visualized on a phosphorescent screen. The deposition on a strip-patterned substrate has been performed. A prototype of the lamp with a nanotube cathode has been designed.

The work is supported by ISTC-1409 project and [in part] by grants INTAS-1701 and 7USP1004100.


Carbon nanotubes have attracted much attention as a promising candidate for field emitters due to their superior properties such as chemical inertness, low thermal and electrical field for electron emission. A direct synthesis of carbon nanotubes on substrates by chemical vapor deposition is one of highly probable routes to reach their application to field emission displays. Several stringent requirements are prerequisite for this purpose, including low temperature growth below 600°C to use glass substrates and large-area deposition for practical use. This study carried out synthesis of carbon nanotubes by chemical vapor deposition on large area glass substrates with an Al cathode using 307 (297 x 210 mm2) at temperatures as low as 550-600°C. Carbon nanotubes were grown by thermal decomposing of CO and H2 gases at an atmospheric pressure. A Ni-Co-Cu alloy was used for a catalyst layer. Preparation of catalyst alloys had a strong effect on the growth of carbon nanotubes. Their correlation was investigated by X-ray diffraction, field emission Auger electron spectroscopy, scanning electron microscopy, transmission electron microscopy, etc. The catalyst film with different compositions are used for the growth of carbon nanotubes. The relative composition of each elemental of the catalyst alloys on nanotube growth morphologies, their diameters, and diffusion of carbon atoms, were studied. Their field emission characteristics are discussed in detail as well.

Z6.9 PRODUCTION AND CHARACTERIZATION OF MoS2 NANOSTRUCTURES BY ELECTRON IRRADIATION D.H. Galvan, Centro de Ciencias de la Materia Condensada UNAM Ensenada, B.C., MEXICO; R. Rozel, Escuela de Ingeniería Química, Universidad Michoacana de S.N.H. Ciudad Universitaria, Morelia, Michoacan, MEXICO; E. Ader, Instituto de Física-UNAM, Mexico DF, MEXICO.

In this work we report the formation of nanotube structures in MoS2 also known as Drysdaleite. The initial samples were obtained from commercial powders (Alfa-Aesar 99.9% pure) of MoS2. Afterwards,
the material was irradiated with electrons on a 2 MeV Van de Graaf accelerator. The irradiation conditions were the following: 1.3 MeV, 5 microamps, 5 minutes, total absorbed dose 25 kGy. The damage was examined in radiochromic films (FWT-80). X-ray analyses were performed in a Philips XRD/XPERT system using Cu Kα radiation at 40 kV voltage and 45 mA current. For transmission Electron Microscopy (TEM) observations, samples were grounded in an agate mortar and placed on carbon coated copper grids. The microscope was a JEOL JEM-2010 with a point to point resolution better than 0.18 nm. We found nanotubes of different sizes and onion-like structures of different sizes and shapes of MoS2 by electron irradiation.

Z6.10 Abstract Withdrawn.

Z6.11 Abstract Withdrawn.

Z6.12 Abstract Withdrawn.

Z6.13 THERMOGRAVIMETRIC ANALYSIS OF C60 INCORPORATED INTO SINGLE-WALL CARBON NANOTUBES (SWNTs).
Masako Yashima, Mifeng Zhang, Yoko Kasaya, ICIORP, Japan Science and Technology Corporation, Tsukuba, JAPAN; Stenji Bundarv, Meijo Univ., Nagoya, JAPAN; Sumio Ishida, Meijo Univ., Japan Science and Technology Corporation, NEC, Tsukuba, JAPAN.

Molecules of C60 are easily incorporated into single-wall carbon nanotubes (SWNTs), and they are well stabilized so they do not escape even when heated at high temperatures in vacuum. When these single-wall carbon nanotubes are heated at 1270 K, the C60 molecules coalesce, instead of escaping from the SWNTs, and form another SWNT inside the sheath SWNT, resulting in double-wall carbon nanotubes. Thus it is apparent that the interaction between C60 and SWNT is not weak. However, the stability of the peapods itself is not well known. To clarify the chemical stability of peapods, we performed thermogravimetric analyses (TGA) in oxygen gas. SWNTs produced by laser ablation were treated with nitric acid and oxygen gas, and C60 was incorporated into SWNTs in the gas phase at 670 K. TGA showed that the burning temperature of SWNTs and peapods differed slightly. However, when SWNTs were heated at 670 K prior to C60 incorporation, the obtained peapods burned at 1020 K, which is 100 K lower than heat-treated SWNTs did. These results suggest that C60 interacted so well with SWNTs that the burning temperature was influenced strongly by defects in the SWNTs.

Z6.14 PROPERTIES OF RAGGED SINGLE-WALL CARBON NANOTUBES INDUCED BY ULTRASONICATION.
Akira Koshio, Masako Yashima, Minfang Zhang, Nanotube Project, International Research Center for Materials Science and Technology Corporation, Tsukuba, JAPAN; Sumio Ishida, Department of Physics, Meijo University, ICIORP-JST, NEC, Nagoya, JAPAN.

Ultrasonication of single-wall carbon nanotubes (SWNTs) in organic liquids enabled us to react SWNTs with organic materials chemically. The modified SWNTs turned into ragged SWNTs (r-SWNTs) with many defects in the sidewall when burned in oxygen. The FT-IR spectra indicated that SWNTs reacted chemically with MCB and PMMA after ultrasonication. For the SWNTs/MCB reactants, three peaks were observed. The peak at 1279 cm⁻¹ corresponds to a C-O stretch of a C=C double bond or a C≡O bond in carbonyl groups. The other two peaks, at 3658 and 2920 cm⁻¹, correspond to the stretching mode of C-H bond in saturated hydrocarbons. Ultrason and carbo decomposes SWNTs and organic molecules, and form defects in the sidewalls and reactive species. The reactive species reacted with SWNTs easily in the solvents. For the SWNTs/PMMA/MCB reactants, two additional peaks were observed, at 2940 and 2850 cm⁻¹. We think that the sonochemical reaction of SWNTs and organic materials is a simple method to functionalize SWNTs. r-SWNTs have some interesting properties, unlike normal SWNTs. They were degraded at 780°C in a vacuum (10⁻7 Torr), and disappeared after heat-treatment at 1200°C for 1 h. We suggest that the holes and defects in the r-SWNTs were formed by oxidation of chemically damaged sites formed during the ultrasonication in organic liquids. We will report analysis of fragments of r-SWNTs by mass spectrometry. Shortened and disentangled r-SWNTs are well dispersed in a solution, however, they coiled as bundles due to the strong cohesion between them. The r-SWNTs were added to single-wall carbon nanotubes (SWNTs) homogeneously dispersed. As the result, the entangled and precipitated SWNTs rapidly (about one minute).

Z6.15 CHARGE DENSITY MODULATIONS ON CARBON NANOTUBES AT ROOM TEMPERATURE. Abdou Hannioui, Nanotubes Research Group, AIST, Tsukuba, JAPAN.

We report on the structure and electronic properties of single wall carbon nanotubes tips with atomically spatial resolution. Scanning tunneling microscopy shows topographic images of closed tips with a variety of geometrical structure; these include round, conical, as well as tips with a messy shape. Standing wave pattern of the charge density is observed in form of constructive interference between the electronic states and its reflection on the nanotube tips. Atomically resolved images show asymmetry in the charge density that decay out within 6 nm away from the top. These distinctive tip states do not exist in the tube and are related to the presence of topological defects at tube ends.

Z6.16 MAGNETIC ANISOTROPY OF CERIUM ENDOHDIAL METALLOFULLERENE. Manami Inakuma, Toshiaki Enoki, Tokyo Institute of Technology, Dept. of Chemistry, Tokyo, JAPAN; Haruhi Kido, Hisamori Shinohara, Nagoya Univ, Dept of Chemistry, Nagoya, JAPAN.

The magnetic properties of Ce@C60 metalloc fullerene have been studied. Cerium (Ce) ion, encapsulated in the metalloc fullerene, has a large magnetic anisotropy. Metalloc fullerenees have a ball-shaped spherical cage structure, the interior of which a metal atom is incorporated. The Ce@C60 fullerene therefore has a potential to have a characteristic magnetic material as a molecular magnet. The correlation of the motion with the magnetization of a molecule magnet has been attractive subject. The magnetic susceptibility of Ce@C60 from 2 to 300 K was measured in the solutions with several solvents (ether, ethylene, hydrocarbon) and the dried-up films from some solutions. The magnetization of some frozen Ce@C60 solutions was found to depend on the applied field magnitude. The dependence suggests that the changed field direction is the rotational motion due to magnetic anisotropy of Ce@C60. This result shows that the easy axis for the magnetization of Ce@C60 is caused by the magnetic anisotropy of Ce ion stuck in the metalloc fullerene. Scanning tunneling microscopy (STM) of the magnetic field for Ce@C60 evaporated on substrates is also observed. We discuss and demonstrate the correlation of the rotation with the magnetic anisotropy of Ce@C60 metalloc fullerene.

Z6.17 DOUBLE RESONANT RAMAN EFFECT IN ISOLATED SINGLE-WALL CARBON NANOTUBES: SECOND-ORDER G' BAND. A.G. Souza Filho, J. Joffre, G. Dresselhaus, M.S. Dresselhaus, Massachusetts Institute of Technology, Cambridge MA; Anna K. Swan, M.S. Udu, B.B. Goldberg, Boston University, Boston, MA; J.H. Falster, C.M. Lieber, Harvard University, Cambridge, MA; R. Saito, Department of Electronic Engineering, Hokkaido University, Japan; R. Saito, Universidade Federal de Minas Gerais, Belo Horizonte, BRAZIL.

We report the resonant second-order G’-band Raman spectra for isolated single-wall carbon nanotubes (SWNTs). The G’-band is used to study a new kind of double resonance phenomenon observable only in SWNTs owing to the one-dimensional density of electronic states and the dispersive behavior of the second-order G’-band. By combining these two characteristics, the G’-band profile for some SWNTs consists of two peaks that arise when both the incident and scattered photons are each resonant with different van Hove singularities in the joint density of states. We show how the G’-band profile can be used to get not only electronic but also structural (n, m) information about the SWNT in resonance with E₁₂. An analysis of the single nanotube spectra allows us also to gain further understanding of the second-order G’-band for SWNT bundles.


Previously, we have shown that high purity multiwalled carbon nanotubes can be prepared from a mixture of xylene ferrocene (90 at% C : 1 at% Fe) inside a quartz tube react to ~700 degrees C [1]. In a series of identical runs, 0.5, 1, 2, 3 and 4 grams of melanine were introduced during the growth of MWNTs from the decomposition of the xylene ferrocene mixtures. The changes in the MWNT products were monitored using SEM, high resolution TEM,
and EELS measurements. As increased amounts of melamine were introduced into the reactor, individual multiwalled tubes with ~50 nm walls transformed into a string of nanotubes comprising of 3-5 walls as evidenced by HRTEM studies. For all melamine concentrations used in the experiments, the purity of the products remained high. From the EELS measurements, we estimate an average nitrogen content of ~5% in the transformed MWNTs (or the strings of carbon nanotubes). The MWNTs with parallel graphitic walls has a detectable nitrogen content.


26.19
**G-BAND RAMAN SPECTRA OF ISOLATED SINGLE WALL CARBON NANOTUBES DIAMETER AND CHIRALITY DEPENDENCE.** Antonio G. Sozzani Filho, Gene Dresselhaus, Mildred S. Dresselhaus, MIT, Cambridge, MA; Anna K. Swan, M.S. Unlin, B.B. Goldberg, Boston University, Boston, MA; Marcos A. Pimenta, Ivan, Federal de Minas Gerais, Belo Horizonte, MG, BRAZIL; Charles J. Lieber, Harvard University, Cambridge, MA; Riichiro Sato, Univ. of Electro-Communications, Tokyo, JAPAN.

The radial breathing mode (RBM) and the tangential mode vibrations (forming the so-called G band) are the two main features in the Raman spectrum of single wall carbon nanotubes (SWNTs), with the resonant Raman spectra of the RBM providing the \( n, m \) indices for an isolated SWNT [A. Jorio et al., Phys. Rev. Letters 86, 1118 (2001)]. The G band is a more complex spectral feature. Due to the flagging of the graphite Brillouin zone into the SWNT zone, and to the symmetry breaking associated with the curvature, the G peak in the Raman spectra of graphite splits into several modes with different symmetries in the Raman spectra of SWNTs. In the case of metallic SWNTs, phonon-plasmon coupling changes the line shape of the G band. We studied the Gband resonant Raman spectra of isolated SWNTs prepared by the CVD method on a Si/SiO\(_2\) substrate. From the radial breathing mode spectra we assign the \( n, m \) structural indices for the different \( n, m \) SWNTs, and can thus obtain the G-band line shape dependence on nanotube diameter and chirality, for both semiconducting and metallic tubes. The most intense peak appears around 1500 cm\(^{-1}\) for both semiconducting and metallic SWNTs, independent of diameter and chirality. The frequency of the second most intense peak is given by \( \omega = 1500 + C/\sqrt{d} \), with \( C = 45.8/\text{cm}^2/\text{nm}^2 \) for semiconducting SWNTs and \( C = 79.5/\text{cm}^2/\text{nm}^2 \) for metallic SWNTs. Metallic SWNTs also exhibit a peak at 1800 cm\(^{-1}\). The relative intensity of the G band modes is found to be different from tube to tube, reflecting a chirality and polarization dependence. We discuss results for SWNT bundles based on isolated nanotube results.

**26.20 STRUCTURE AND PROPERTIES OF C\(_{6} \)G/SWNT.** Brian W. Smith, Richard M. Russo, B.C. Sarasvithara, Ferenc Sercel, David E. Luzzi, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA.

Our recent achievement of high-yield C\(_{6} \)G/SWNT synthesis facilities characterization by various techniques, including selected area electron diffraction (SAD) and Raman spectroscopy. The obtained SAD patterns and the interior C\(_{6} \) molecules sit on a single 1-D lattice having a parameter of 0.976 nm. Simulated SAD patterns and real-space measurements both support this determination and do not indicate a lattice with a more complex basis, e.g. a dimer basis. Some evidence is found for variable C\(_{6} \)G/C\(_{60} \) separations. Energy and bulk-filled SWNTs (22%, 55%, and 90% yields) subjected to identical processing steps were examined by room temperature Raman spectroscopy. Systematic differences are seen between the spectra of filled and unfilled SWNTs, particularly with respect to the G and RBM bands of the nanotubes. We present a possible explanation for this behavior.

**26.21 ENCAPSULATION OF AN ISOSTRUCTURAL METALLOFULLENE SERIES: Er, Sc, Zn, Mg, Ca@SWNT (\( x = 1.3 \)).** Richard M. Russo, Brian W. Smith, B.C. Sarasvithara, David E. Luzzi, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA.

The future application of single-wall carbon nanotube systems (SWNTs) depends on the ability to modify their intrinsic properties by manipulating their structure or microstructure. A unique advantage of nanotubular structures is the ability to modify their function through the filling of the nanotubes. We have encapsulated number of high order fullerenes and metallofullerenes such as La\(_{2} \)G and Ca\(_{2} \)G. One of the potentially important goals of these systems is to find an isostructural series in which properties can be modified by chemical substitution. We have found such a system in Er, Sc, Zn, Mg, Ca@SWNT (\( x = 1.3 \)). The structural properties of this system have been studied using high resolution transmission electron microscopy and electron diffraction. It was found that the encapsulated fullerene structures are similar to the original one-dimensional chains with the same periodic spacing. Several interesting observations indicate that the surrounding nanotube can have a profound effect on the stability and chemistry of encapsulated molecules. For example, the encapsulated fullerene molecules remain stable at temperatures above the point at which they would decompose under non-confined conditions. At temperatures which chemical reactions such as the metathesis reaction occur, the nanotube terminates the final product through steric congestion. The thermal stability of these supermolecular assemblies are studied and large variations are found. The behavior is nominally consistent with the mass of the encapsulated metallofullerenes.

**26.22 THERMOdynamic ANALYSIS OF CARBON NUCLEATION ON METAL SURFACES.** Anna K. Swan, Ivan, Federal de Minas Gerais, Belo Horizonte, MG, BRAZIL; Charles J. Lieber, Harvard University, Cambridge, MA; Riichiro Sato, Univ. of Electro-Communications, Tokyo, JAPAN.

An understanding of the formation mechanism on nanotubes is crucial to design techniques for the controlled growth of pure nanotube material. Here we present a thermodynamic analysis of graphite-like carbon nucleation processes on the metal surface. We have considered the mechanisms of catalytic formation of different carbon deposits, such as carbon fibers, multi- and single-wall carbon nanotubes. This contribution is based on the majority of these mechanisms include some common steps. The most important of them is the step of nucleation of carbon on the metal surface. We suggest that the nucleation conditions and thus the critical size of carbon nucleus determine the type of final deposit. On the base of experimental and literature data we have proposed that carbon nucleus has the form of flat saucer with the edges bonded to the metal surface. The consideration of variation in Gibbs free energy provides us a functional dependence between the critical radius of the carbon nucleus and reaction parameters such as reaction temperature, carbon content in a metal-carbon particle and parameters which characterize the nature of metal catalyst. Analyzing the functional dependence of critical radius we can conclude that: a) an increase of the reaction temperature leads to the formation of smaller nuclei and finally to the formation of single-walled nanotubes; b) the use of metals which characterized by a higher metal-carbon energy bond, yields nanotubes with smaller diameters; c) single-wall nanotubes growth is likely to proceed on liquid metal particles; d) elements that decrease the melting point of the catalyst-carbon mixture and do not form stable compounds with carbon at the reaction temperature promote also the formation of single-wall nanotubes. This work was supported by INTAS grant 07-1700.

**26.23 FILLING SINGLE WALLED CARBON NANOTUBES WITH METAL NANOWIRES AND MOLECULAR SPECIES.** B.C. Sarasvithara, Richard M. Russo, David E. Luzzi, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA.

Single walled carbon nanotubes (SWNTs) have hollow channels of 1.4 nm diameter and can be filled with various materials like metals and metal chlorides, fullerenes and metallofullerenes etc. The present exploration involves filling with crystalline and molecular systems. The nanometer dimensions of carbon nanotubes offer an ideal template to synthesize one-dimensional (1D) nanowires and study the size specific properties of various material systems. Nanowires of magnetic metals (e.g. Fe, Co) have been synthesized by the sealed-tube reaction and solution phase method involving the metal chlorides and SWNTs. The nanowires have been imaged using high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM). The STEM imaging complements the HRTEM imaging in terms of the contrast mechanism wherein the image contrast is solely decided by the scattering cross section, which is proportional to \( Z^2 \). The properties of the nanowires have been studied by carrying out magnetic measurements. Several molecular species have been investigated to determine whether they fill the interior of the SWNTs by the vapor or liquid phase filling process and have been characterized using HRTEM and STEM imaging as well as electron energy loss spectroscopy (EELS). The interaction of SWNTs with molecular materials such as the porphyrins has also been studied and will be reported.

**26.24 RAMAN EXCITATION PROFILES IN CARBON NANOTUBES.** M. Cimino, J. Mendez, Dept. of Physics and Astronomy, Arizona State University, Tempe, AZ; H.P. van der Meulen, J. Callizo, J.
Raman excitation profiles (the laser photon energy dependence of the Raman intensity) for the radial breathing mode of many carbon nanotubes have been measured using tunable dye lasers. The experiments were performed at helium and at room temperature and as function of an applied magnetic field of up to 12 T. From these measurements it is possible to determine optical transition energies in nanotubes with sub-KHz frequency resolution. These results provide the most stringent test of the predicted electronic structure of the tubes. We also discuss the effect of chirality and bundling on the Raman excitation profiles.

**Z6.25** STUDY OF THE RAMAN D-BAND IN ISOLATED SINGLE-WALL CARBON NANOTUBES. M.A. Pimenta, Departamento de Física, Universidade Federal de Minas Gerais, BRASIL; A. Jorio, S.D. M. G. Souza Filho, G. Dresselhaus, M.S. Dresselhaus, Department of Physics, MIT, Cambridge, MA; J.H. Hafner, C.M. Lieber, Department of Chemistry, Harvard University, Cambridge, MA; R. Saito, Department of Electronic Engineering, University of Electro-Communications, Tokyo, JAPAN.

Raman D-band spectra are reported for several different isolated SWNTs using different laser energies. At a fixed laser excitation energy $E_{\text{exc}}$, the different isolated SWNTs actually exhibit different D-band frequencies $\omega_D$. However, the mean value of $\omega_D$ for isolated SWNTs depends on $E_{\text{exc}}$, similar to the general case of $sp^2$ carbon materials, and this mean value of $\omega_D$ obeys the same dependence $\omega_D(E_{\text{exc}})$ that is observed for SWNT bundles. The observed $\omega_D$ dependence of $\omega_D$ and the corresponding D-band intensity $I_D$, for isolated tubes suggests that the associated phonon modes are not the center of the 1D SWNT Brillouin zone (BZ), and each different laser energy probes different SWNTs and phonons with different wavevectors within the interior of this 1D BZ, similarly to $sp^2$ carbons. These phonons become Raman-active due to the finite size of the SWNTs or to the presence of defects, which break the translational symmetry along the nanotube axis, explaining the fact that $I_D$ appears to be random from one nanotube to another. By comparing the Raman spectra of the D-band with that of the tangential $G$-band for different SWNTs probed with a given $E_{\text{exc}}$, it is shown that $\omega_D$ decreases with increasing nanotube diameter $d$ for both semiconducting and metallic tubes. Moreover, we observed that $\omega_D$ for metallic SWNTs is in general higher than $\omega_D$ for semiconducting SWNTs at the same $E_{\text{exc}}$ value. Finally, we argue that the anomalous $\omega_D(E_{\text{exc}})$ plateau behavior observed for SWNT bundles can be explained by considering the diameter dependence of $\omega_D$ for isolated SWNTs and the resonant nature of the Raman process.

**Z6.26** OPTICAL LIMITING CHARACTERISTICS OF PURE, B- AND N-DOPED MULTI-WALLED CARBON NANOTUBES. J.F. Xu, R. Cerver, D.L. Carroll, Department of Physics, Clemson Univ., Clemson, SC, M. Terrones, N. Grabot, M. Reyes-Ramos, Fullerene Science Center, CPECS, Univ. of Buffalo, Buffalo, UNITED KINGDOM, H. Terrones, IFIC, UC San Diego, UC San Diego, United States, P.M. Ajayan, Dept. of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY.

Optical limiting characteristics of pure, B- and N-doped, multi-walled carbon nanotube suspensions are compared. The non-linear measurements were made with 8 ns pulses for the 532 nm and 1064 nm lines of a Nd: YAG laser using an f/15 optical system. The onset of non-linearity was observed to occur at a lower fluence in the doped carbon nanotube suspensions than in the pure carbon tubes case. Further, the doped nanotube materials exhibit a stronger overall nonlinear response with fluence than pure carbon tube suspensions. Carbon black suspensions (CBS), and n-carbon suspensions (NCS). These results suggest that the limiting mechanisms are quite sensitive to the electronic effects of the dopant on the nanotube.

**Z6.27** A NEW CLASS OF CARBON NANOCONES. Szelinski Dimowski, Yuriy Gogotsi, Drexel Univ., Dept. of Materials Engineering, Joseph Libera, Northwestern Univ., Dept. of Materials Science and Engineering, Evanston, IL.

A new class of low-angle conical carbon structures has been discovered. These nanocones were first found in pores of glassy carbon along with cylindrical nanotubes and graphite polyhedral crystals [giant polyhedral nanotubes]. While cylindrical nanotubes become polyhedral when their diameter exceeds a certain critical value, no polyhedralization of the cones has been observed even for the largest diameters. Basically, the crystals are conical carbon nanotubes with thick graphite walls and semipheral tips. Besides the perfect structure, these graphite cones differ from any carbon cones observed earlier by much smaller apex angles, sometimes less than 3 degrees. The largest cones reach 2-3 microns in length, although most of them are in the sub-micrometer range. Transmission electron microscopy (TEM) and selected area electron diffraction show well-ordered graphite walls. Preliminary results show electrical conductivity, strength, and chemical stability of these crystals. Large-scale synthesis of nanocones and their potential application as tips for scanning probe microscopes or electron emitters are discussed.

SESSION 27: CHARACTERIZATION OF NANOTUBE SYSTEMS [LIMITS AND CHALLENGES]

Chair: Elena D. Olivastro and Marcos A. Pimenta

Wednesday Morning, November 28, 2001

[Session continued...]

8:30 AM Z7.21 RAMAN SPECTRA FOR ONE CARBON NANOTUBE. M.S. Dresselhaus, MIT, MA; R. Saito, U. Electro-Comm., TOKYO; A. Jorio, MIT, MA; A.G. Souza Filho, MIT, MA; M.A. Pimenta, Universidade Federal de Minas Gerais, Belo Horizonte, BRASIL, G. Dresselhaus, MIT.

A brief review is presented of the new science connected with the phonon spectra of single wall carbon nanotubes (SWNTs) as observed by Raman spectroscopy, and the information about carbon nanotubes provided by Raman spectroscopy. The very sharp one-dimensional density of electronic states in small diameter SWNTs and the strong electron-photon coupling allow observation of the Raman spectra from one isolated SWNT when the incident and/or scattered photon is in resonance with an interband transition $E_i$, between van Hove singularities in the density of states of tubes between the nanotube valence and conduction bands. Observation of the Raman spectra of the radial breathing mode from one isolated SWNT is used to provide a definitive identification of its structure through determination of the nanotube ($n, m$) indices. Variations of this basic concept for different situations for semiconducting and metallic nanotubes are discussed. This information is further used to determine to high resolution the profile of the joint density of states near a van Hove singularity. Because of the high sensitivity of the electron, transport, vibrational and other nanotube properties to the structural ($n, m$) indices, this non-destructive, readily available characterization technique is expected to have a significant impact on current basic research on carbon nanotubes. Examples of spectra and polarization effects in SWNTs are reviewed briefly.


Carbon nanotubes systems have revealed large potentialities in terms of applications, especially at a nanometric scale. As a consequence, the different interactions which can take place can be of primary importance. In this paper, we report studies carried out on different carbon nanotubes systems such as SWNTs, MWNTs and polymer/nanotubes composites. By using Raman spectroscopy via the Raman and TM, apart from the expected interactions between tubes in bundles which have initiated experiments on individual entities, we put in evidence strong chemical reactions at the interface metal/nanotubes whenever Ag or Au surfaces are used to carry out SERS experiments. We show in particular that a different behavior is observed for metallic and semiconducting tubes. Also, a high state of disorder is observed, together with the transformation of nanotubes to other carbon compounds. In the case of MWNTs, theoretical calculations allow us to interpret the low frequency Raman modes by introducing interactions in concentric tubes, in rather good agreement with experiments. Finally, in polymer/nanotubes composites, an upshift of the Raman is observed and we show in this case that it originates from the dynamical stress applied by the polymer on the bundles in response to the breathing vibration. This work has been carried out in the frame of the EEC programme COMELAN, HPRN-CT-2000-00128.

9:30 AM Z7.23 ORIENTATION DEPENDENCE RAMAN STUDY OF VERTICALLY ALIGNED CARBON NANOTUBES. D. Brys-M...
Aligned carbon nanotubes (ACNTs) grown by direct current plasma enhanced chemical vapor deposition (DC PECVD) using acetylene and ammonia are of technological significance for low-dimensional electronics. The advantage of PECVD is that it is a controllable and deterministic catalytic growth process. Thus, the growth location of the nanotube is precisely determined by the location of the catalyst on the substrate. High temperature plasma was used to determine the structural characteristics of the aligned nanotubes as well as the degree of alignment. The Raman spectra obtained from ACNTs were compared with numerous other forms of carbon. In our case, the G band intensity was found to be dependent on the alignment of the tubes with reference to the polarization of the incident light in VV configuration as reported for MWNT by Rao et al [1]. The observed variation of G band intensity for MWNT is different from that reported for SWNT. This is attributed to the difference in the absorption characteristics of polarized light between MWNT and SWNT due to difference in their depolarization effects. Also, such dependence was not observed in carbon fibers. Therefore, this technique can be used as a non-destructive 'acid' test for determining the degree of alignment as well as confirming the tubular nature of PECVD of ACNTs.

Reference:

9:45 AM Z7.4
ELECTRICAL AND THERMAL PROPERTIES OF SINGLE WALL CARBON NANOTUBE FIBERS. Jun-Jung Vayro, Marc C. Ilagono, Michael Bierzak, Alan T. Johnson, John E. Fischer, Univ. of Pennsylvania, John H. Poulton, CRPP Bordeaux, FRANCE; Roy Baughman, Honeywell International, NJ.

We measured the electrical and thermal properties of single wall carbon nanotube (SWNT) fibers prepared using a recently developed technique [B. Vigo et al., Science 290, 1331 (2000)]. Non-metallic behavior from 1.4 to 300 K has been observed from the resistivity measurements. Heat treatment at 400°C results in a decrease of resistivity by as much as three orders of magnitude. Further studies on heat treatment will be reported. The room temperature thermal conductivity ranges from 15 to 70 W/mK in different samples. These values lie between those of bulk unoriented metals (10 W/mK) and magnetically-aligned SWNT films (250 W/mK). This result indicates that some alignment of the tubes occurs during fiber formation. The thermoelectric power resembles that of SWNT: n-type; positive and moderately large (~40 μV/K) at room temperature.

10:30 AM Z7.5
STRUCTURAL CHANGES IN SINGLE-WALL CARBON NANOTUBE BUNDLES UNDER PRESSURE. Stephanie Role, Intense Pulsed Neutron Source, Spallation Neutron Source, Argonne National Laboratory and Rouge de Dynamique des Phases Condensées (UMR CNRS 5581), Université Montpellier II, Montpellier Cedex 5, FRANCE; Jean-Louis Sauvajol, R. Almaini, Groupe de Dynamique des Phases Condensées, Université Montpellier II, Montpellier Cedex 5, FRANCE; Igor Goshchenkov, Russian Research Center "Kurchatov Institute", Moscow, RUSSIA and Laboratoire Léon Brillouin (CEA/ CNRS), CE Saclay, Giuas-Veeye Cedex, FRANCE; Isabelle Mirebeau, Laboratoire Léon Brillouin (CEA/CNRS), CE Saclay, Giuas-Veeye Cedex, FRANCE.

The pressure-induced structural changes of single-wall carbon nanotubes organized into 3D crystalline bundles are studied by neutron diffraction up to 50 kbar. The pressure dependence of the position of the (10) Bragg peak is found to depend on the orientation of the nanotube bundle with respect to the diffraction plane. This behavior implies the presence of an unusual pressure component along the axis of the nanotube. The pressure dependence is well described in the framework of a pressure-induced progressive deformation of the tube section, from circular to hexagonal, in addition to the van der Waals compression.

10:45 AM Z7.6
BINARITY EFFECT OF LAYERED NANOTUBES. Raymond Whitby, Wen Kung Hsu, Department of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, UNITED KINGDOM; Chris Boothroyd, Department of Materials Science & Metallurgy, University of Cambridge, Cambridge, UNITED KINGDOM; Peter Porco, David Walton, Harold Kroto, Department of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, UNITED KINGDOM.

Pyrolysis of multi-walled carbon nanotubes (MWCNs) with thin coatings of tungsten oxide, in H₂/N₂, generates a binary phase of layered nanotubes in accordance with the template effect, where tungsten dioxide coats the MWCNs.

11:00 AM Z7.7
CRYSTALLIZATION OF FULLERENE IN QUASI-ONE DIMENSIONAL NANOSPACE: C₆₀ IN DOUBLE WALL CARBON NANOTUBE. Koen Hirahara, Nanotubities Project, Japan Science and Technology Corp., c/o Meijo Univ., JAPAN; Shunji Bando, Dept. of MSEE, Meijo Univ., Nagoya, JAPAN; Toshiro Nakashita, Konan University, Dept. of Metallurgical Engineering, Meїn Univ., Tsu, JAPAN; Sumio Iijima, 'Nanotubities' Project, Japan Science and Technology Corp., Dept. of MSEE, Meijo Univ., Nagoya, JAPAN.

In the most studies of fullerene encapsulated nanotubes (so-called peropods) reported so far, the SWNTs used have a suitable inner diameter for aligning the fullerene molecules one-dimensionally in the intertubular space. In this study, we used SWNTs with the diameter larger enough than the diameter of fullerene molecules for making peropods. The fullerene in such large diameter tubes were also packed regularly and had a certain crystal structure. The internal space for such large diameter tube with respect to the diameter of fullerene is regarded as the quasi-one dimensional nanospace for the arrangement of fullerene molecules. In one-dimensional nanospace realized in 1.4 nm tubes, the intermolecular spacings of various fullereones were different from the values of 3D crystals due to the interactions between the fullerene and also between the fullerene and the surrounding tube-wall. In the quasi-one dimensional nanospace, the difference of such interactions is possible and control the intermolecular spacing. Because the fullereones were not surrounded by the tube-wall. In the present study, we used arc derived double-wall carbon nanotubes (DWWNTs) which have mean inner diameters of ca. 3 nm. Encapsulation of fullereone were carried out by the vapor phase reaction. High-resolution electron microscopy (HRTEM, JEM-2010F, 120KV) imaging and electron diffraction method were employed to characterize the crystal structure of the fullereones. In most of TEM images observed, the fullereone chains seen in the tubes were close packed and aligned along the tube-wall, and formed bundle structure in the tube. The structural model for them and the diffraction pattern of the quasi-one dimensional fullerene crystal in DWWNT are going to be discussed on the poster.

11:15 AM Z7.8
FILLING SINGLE-WALL CARBON NANOTUBES (SWNTS) WITH METALLOGENES: A FIRST NON-FULLERENE HYBRID MOLECULAR SYSTEM. Jerome Steren, David E. Luzzi, University of Missouri Science and Engineering, Philadelphia, PA; Norbi M. Nemes, University of Pennsylvania, Department of Physics, Philadelphia, PA.

One of the unique features of carbon nanotubes is their structurally and chemically well-defined interior space. This allows for the synthesis of a range of materials in which the lumen is filled, or partially filled, with other materials; ionic compounds, alkali metal fullereones. These hybrid structures provide the possibility to modify the properties of the nanotube and for the filling species. The use of molecular-based hybrid systems created to date are fullereones and metalfullereones encapsulated in SWNTs. Here we report the synthesis and analysis of molecules (ferrocene, chromocene, vanadocene) encapsulated in SWNTs. In the case of ferrocene, the effective filling of the SWNTs was accomplished from both the liquid and the vapor phase. The other two metalloenes were filled from the vapor phase. High resolution transmission electron microscopy reveals single molecular chains of metalloenes inside SWNTs. Molecules move under the electron beam in the SWNTs indicating the absence of strong chemical bonds between each other and the SWNT wall. Their movement freezes after short illumination which is the result of irreversible damage. Energy dispersive X-ray spectrometry confirms the presence of iron, chromium and vanadium.

11:30 AM Z7.9
MAGNETIC PROPERTIES OF METALLIC FULLEREONES ENCAPSULATING IN SINGLE-WALL CARBON NANOTUBES. Shunji Bando, Meijo University, Dept of Materials Science and Engineering, Nagoya, JAPAN; Koen Hirahara, Japan Science and Technology Corporation, Nagoya, JAPAN; Haruhiko Kato, Toshiro Nakashita, Konan University, Department of Chemistry, Nagoya University, Nagoya, JAPAN; Sumio Iijima, Japan Science and Technology Corporation, NEC Corporation, Tsukuba and Meijo University, Nagoya, JAPAN.

Magnetization curves of C₆₀C₆₀ encapsulated single-wall carbon nanotubes were measured by SQUID susceptometer with the magnetic field up to 7 T. According to the magnetization curve analysis, it was found that the total quantum number of C₆₀ nanotubes was S = 7/2 and the spin quantum number of C₆₀ cage would be S = 1/2 down to
practical purposes, while metallic chiral nanotubes undergo a bending-induced metal-semiconductor transition that manifests itself in the occurrence of effective metal contacts. This experiment demonstrated the possibility of forming intra-tube junctions and conducting electrical contacts via the recombination of open-ended NT's that are in close proximity to each other. Finally, we will examine the behavior of nanotube-metal contacts and explain the anomalously large contact resistance observed in nanotube devices as due to the spatial separation of their conductance eigenchannels. The results for various contact geometries and strategies for improving device performance will be discussed.

2:15 PM *28.3*

WATER CONDUCTION THROUGH CARBON NANOTUBES

C. Bein, National Institutes of Health, Laboratory of Chemical Physics, NIDDK, Bethesda, MD; Jayendra C. Ranasinghe, Jerey P. Noworyta, University of Maine, Department of Chemistry, Orono, ME

The interactions of small, un-capped carbon nanotubes with water are studied by long molecular dynamics simulations. Water is found to penetrate the nanotube interior, forming well-ordered hydrogen-bonded water chains. Water penetration is sensitive to details of thermodynamic conditions and interaction potentials, resulting in sharp, first-order like transitions between filled and empty states. Under wetting conditions, water molecules are transported efficiently through nanotubes. Implications on the design of nanotube channels for small molecules and protons will be discussed.

2:45 PM *28.4*

CHARGE CARBON NANOTUBES. P. Kubinski, P.M. Ajayan, Material Science and Engineering Department, S. Nagy, Physics Department, Remsenschpol Polytechnic Institute, Troy, NY, and P. Zippol, Materials Science Division, Argonne National Laboratory, Argonne, IL

Ab-initio calculations of charge distribution on negatively and positively charged carbon nanotubes result in charge distribution profiles with a significant increase of charge density at tube ends, in quantitative agreement with classical electrostatic analysis, even for tubes with a single electron total charge. Using density-functional-based tight-binding simulations with self-consistent charge density, we study structural, mechanical and electrical response of the tube to the charge, and identify the maximum value of charge at which the tube is stable. This result in combination with classical electrostatic analysis allows us to determine a simple analytical dependence of the stability criterion on the tube length. We also calculate related critical value of the electrostatic potential and discuss differences between closed and open ended carbon nanotubes.

This research was supported by Phillip Morris USA P.Z. acknowledges support by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

3:15 PM *28.5*

NANOMECHANICS OF NANOTUBES AND NANOTUBE-POLYMER COMPOSITES. Deepak Srivastava, Computational Nanotechnology, NASA Ames Research Center, CA; Chengwu Wei and Kyungmi Cho, Department of Mechanical Engineering, Stanford University, CA

Recently carbon nanotubes are considered as nanoscale fibers that can strengthen polymer composite materials. Nanotube-polymer composite materials can be used for micron scale devices with designed mechanical properties and smart polymer coating to protect materials under extreme physical conditions. To explore these possibilities it is important to develop a detailed atomic scale understanding of the mechanical coupling between polymer matrix and embedded nanotubes. In this talk we will describe the physical, mechanical and chemical properties of polymer matrix and carbon nanotube interfaces using molecular dynamics. The density of the CNTs in a fiber composite, as a function of cooling rate, is found to change significantly above glass transition temperature indicating the formation of a high thermal expansion coefficient material above glass transition temperature. The thermal conductivity of polymer-nanotube matrix also depends significantly on thermal conductivity of nanotubes and of polymer matrix. The mechanical load transfer for very small strains lead to up to 30% increase in the value of the Young's modulus of the composite, it is found that limiting strain for non-bonded interactions can be increased by mechanical strain-relaxation cycle of the composite. The load transfer is studied as a function of the angle of inclination of the nanotube within the matrix fibers, and processing of the composite through strain-relaxation cycles lead to a more favorable bonding between polymer molecules with the nanotubes. Study shows that the bonding between polycatylene and CNT is energetically favorable. Chemical bonds can be formed at multiple sites, which makes the mechanical load transfer from the polymer chain to the tube more favorable.
chemical coupling between CNTs and polymer matrix on the mechanical properties of the composite and the tubes.

3:45 PM Z8.6
INTERACTION OF SMALL MOLECULES AND RADICALS WITH CARBON NANOTUBES. Sunoj K. Nayak, Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, NY.

We have studied the interaction of small molecules like O$_2$, NO$_2$, CO and radicals like NO, N$_2$O, O$_3$ with a working gas nanotube interface using first-principle density functional theory. We find that the presence of NO, N$_2$O, O$_3$ and radicals like NO, N$_2$O, O$_3$ does not affect the gas-solid contact or bonding of the molecules. The interaction of gas molecules with the nanotube interface is studied using first-principle density functional theory. We find that the presence of NO, N$_2$O, O$_3$ and radicals like NO, N$_2$O, O$_3$ does not affect the gas-solid contact or bonding of the molecules.

4:15 PM Z8.7
SELECTIVE PARTITIONING OF HYDROPHILIC SOLUTES INTO CARBON NANOTUBES Amrik Kalra$, TuLin Ghosh$, Gerhard Hummel$ and Skelifar Garcia$. Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY. $Laboratory of Chemical Physics, National Institutes of Health, Bethesda, MD.

Much of the interest in carbon nanotube research stems from their unique mechanical and electrical characteristics and resulting mechanical, structural, electronic, and optical properties. We have recently studied the interactions of hydrogen bonded water molecules in aqueous solutions of hydrophilic solutes. We find that the interior of carbon nanotubes is highly selective to partitioning of hydrophilic solutes. The partitioning process is fast and occurs over time scales of 1 to 2 nanoseconds. Kinetics of selective partitioning process are obtained by performing several tens of simulations started from different initial conditions. These studies point to future applications of functionalized carbon nanotubes as sensing and/or separation devices that are highly selective to specific molecules of interest.

4:40 PM Z8.8
LARGE SCALE AB INITIO INVESTIGATION OF LITHIUM DIFFUSION IN CARBON NANOTUBES. Vincent Meunier, Christopher Roland, Jerry Bermudez, North Carolina State University, Department of Physics, Raleigh, NC.

It is well known that the performance of Li-ion batteries depends directly on its intrinsic capacity (i.e., the Li/C uptake ratio) which for Li-graphite systems is ideally 372 mAh/g (LiC$_6$). Recently, there has been considerable interest in carbon nanotube systems as providing a suitable alternative to graphite as an intercalation material. Because of their unique structure, nanotubes may provide for an increased Li uptake ratio of 1:2. This is the ideal case in which, in addition to the interstitial space available between nanotubes, the interplanar regions of the nanotubes may be accessed. With large-scale ab initio simulations we have therefore investigated Li adsorption both on and into, isolated carbon nanotubes and nanotubes ropes. Specific issues addressed include the effect of metallicity on Li adsorption, charge transfer effects, dynamics of Li motion, and different pathways for the ions to enter nanotubes interiors. Our calculations show that only in the presence of open nanotubes, or nanotubes with topological defects with 8 (or higher) membered rings can the ions enter readily. These results are consistent with recent experiments which show that Li uptake is greatly enhanced if the nanotubes are initially processed via halogenation. To complement these static calculations, we have also directly simulated the long-time motion of Li ions in nanotube systems using a frozen charge density molecular dynamics approximation.

4:45 PM Z8.9
DETAILED GEOMETRIES AND THEIR IMPORTANCE TO THE ELECTRONIC PROPERTIES OF CARBON NANOTUBES. Kenjiro Kamatani, Sasaami Sato, Tokyo Institute of Technology, Dept of Physics, Tokyo, Japan.

In the framework of the density-functional theory (DFT), we study geometries and the electronic structure of so-called zig-zag carbon nanotubes with various diameters. From the total-energy calculation their structural parameters are completely optimized. Interestingly, there are two kinds of bonds which are found to be considerably different from each other, with strong tube-diameter dependences. Also the two kinds of bond angles show different diameter dependences. The electronic bands of zig-zag carbon nanotubes are found to show sizeable changes from that of initial “ideal geometry” nanotubes with uniform bond lengths. This indicates the importance of the detailed geometries in discussing the electronic properties of carbon nanotubes. We also show an interesting difference of the energy gap values between the present DFT results and the previous tight-binding results.

SESSION 29 POSTER SESSION
MODELING, ENERGY STORAGE, ELECTRODE APPLICATIONS, AND CHEMICAL MODIFICATIONS
Wednesday Evening, November 28, 2001
8:00 PM
Exhibition Hall D (Hynes)

29.1 MECHANICAL BEHAVIOR OF CARBON NANOTUBES FILLED WITH METAL NANOWIRES BY ATOMIC SIMULATIONS. D. Dunic, P. Kebabchi, P.M. Ajayan, MSE Department and S. Nagy, Physics, Applied Physics and Astronomy Department, Rensselaer Polytechnic Institute, Troy, NY.

Using molecular dynamics simulations we studied mechanical behavior of (10,10) carbon nanotubes filled with nanowires. The elastic properties, as well as failure mechanisms were determined by simulating three point bending test, pressing the center of relatively long tube with a moving hard repulsive cylinder crossed at 45° with respect to the tube, while supporting the tube ends with fixed cylinders. We found that following elastic response, at larger deformation, the metal wire yields well before the carbon bonding is affected. The behavior of filled tubes was compared with that of hollow tubes. We also simulated indentation of filled tubes residing on a hard flat surface. Similarly as in the bending test, metal wire yields first, is cut in half along its cleavage plane and pushed away from the indenter. Upon further increase of the indentation force, carbon tube is broken and forms two open ends that are rapidly zigzag around the cut metal wire. Remarkably, the shape of the zigzag tube end is similar to a sharply cut cylinder at about 45° angle and appear to be determined by the shape of the metal wire cleavage. This result imply a possibility of designing tubes with various closed end shapes using nanoscale manipulation procedures.

This research was supported by Phillip Morris USA.

29.2 MODEL BROAD NANO TUBES RELATED TO C$_{26}$, C$_{32}$ AND C$_{40}$ COMPUTATIONAL INSIGHT. Zdenek Sminia, Filip Uhlik, Tomek Simka, Filip Uhlik, Toyohashi Univ of Technology, Dept of Knowledge-Based Info. Engn., Toyohashi, JAPAN; Charles Univ, Dept of Phys. and Macromol. Chem., Prague, CZECH REPUBLIC.

Very recently, narrow nanotubes have been observed with a diameter of 1-2 A (Shin$ et$ al.,$ Nature$ 405$ (2000)$ 586$ and even with a diameter of 4 A (Qin$ et$ al.,$ Nature$ 408$ (2000)$ 50$). It has been supposed that the narrow nanotubes are closed by fragments of C$_{26}$ and C$_{32}$ fullerenes. The contribution calculations on related model nanotubes with stoichiometries like C$_{4n}$, C$_{6n}$ or C$_{8n}$. Computations are carried out at the PM5, SAM1, and B3LYP/6-31G* levels. Two C$_{36}$ fullerenes are considered, D$_{3h}$ and D$_{4h}$ and, for example, at the PM5 level and with the C$_{4n}$ nanotube stoichiometry the D$_{4h}$ cage closure gives a lower energy (by 185 kcal/mol and diameter of 3.42 A). There is another possible cage, C$_{32}$ cage with a D$_{4h}$ symmetry. At the PM5 level and with the C$_{4n}$ nanotube stoichiometry the D$_{4h}$ closure has the nanotube energy lower by 210 kcal/mol (with the nanotube diameter of 5.43 A) compared to the D$_{3h}$ nanotube closure. On the other hand, four-membered rings should not play a significant role in the narrow nanotubes with the diameter of 4 A, where the dodecahedron-related closure should be exclusive. The findings are also supported by the B3LYP/6-31G* calculations.


In the framework of the density-functional theory (DFT), we study geometries and the electronic structure of so-called zig-zag carbon nanotubes with various diameters. From the total-energy calculation their structural parameters are completely optimized. Interestingly, there are two kinds of bonds which are found to be considerably different from each other, with strong tube-diameter dependences. Also the two kinds of bond angles show different diameter dependences. The electronic bands of zig-zag carbon nanotubes are found to show sizeable changes from that of initial “ideal geometry” nanotubes with uniform bond lengths. This indicates the importance of the detailed geometries in discussing the electronic properties of carbon nanotubes. We also show an interesting difference of the energy gap values between the present DFT results and the previous tight-binding results.
Symmetry breaking in the electronic and phonon structures of carbon nanotubes is considered theoretically, especially for the possible functionalization of nanotubes by the defects observed in the 1-D band of Raman spectra, the absence of back scattering, and chemical reactions. A key idea for such defects is that the eigenstates of the electron or phonons become localized by collecting a range of k vectors near the Fermi level. As a result, the amplitude of the eigenvectors would be locally large and give a better sensitivity to various quantum physical properties. The localization phenomena should depend on the geometrical shape of the defect. Here we present recent calculated results for the physical origin of the D-band and G-band. Electron-phonon coupling around the defect becomes strong because band-phonon states have a large amplitude. Another key issue for such defects is that the defect may be essential for scattering since it affects the transport properties of both electrons and phonons. We propose to characterize the size and the depth of the scattering as a function of the defect size. We have previously shown that back scattering by electrons. We here apply the effects of defects on phonon scattering. An anomalous thermal conductivity, which affects single nanotube spectroscopy, might be related to this scattering. We gratefully acknowledge the support of NSF grant DMR-98-04743, and the grant of Ministry of Education (No.1344081).

**20.4 ENERGETICS OF FINITE, OPEN ENDED, SINGLE WALL BORON NITRIDE AND CARBON NANOTUBES**

Marian W. Rice, Philip V. Smith, School of Chemical and Physical Sciences, The University of Newcastle, Callaghan, NSW, AUSTRALIA; Yoshitsugu Kawai, Institute for Materials Research, Tohoku University, Sendai, JAPAN

Determination of the optimum, energetically favourable atomic structure of nanotubes (NT) is essential for any 'smart' application of NTs. This includes the knowledge of the diameter variation of NTs, as well as the interaction of kinks and other possible defects. Despite the large number of experimental and theoretical studies performed for Carbon NTs (CNTs) the collected data indicate that while the atomic structure of CNTs is relatively simple and easy to describe, it is, however, purely understood. Among the successfully synthesised non-carbon tubes, the BN nanotubes (BNNT) are usually considered to be structural analog of CNTs. Recent studies have suggested, however, that this relationship is complicated. As a result, the 'zigzag' shell helicity of BN NTs is a favourable shell structure of BN NTs assemblies. This domination has been observed in the tube structures produced by different methods (laser heating at high pressures, thermal or chemical processes), in analogy on some kind of universal behaviour of BN NTs. This experimental fact is, however, in sharp contrast to CNT for which the structure analysis of CNT assemblies indicates on no preferred shell helicity of the formed tubes. It is easy to understand that the shell chirality is partly related to the topology of edge of the open ends of the ideal, finite tubes. In this paper we want to report on our Tight Binding total energy calculations for clean, ideal, open-ended BN tubes where the relationship - the open edge of the BN NT with different chirality vs mechanical (strain energy) of the infinite tubes with the same chirality - has been explored. The analog calculations performed for CNTs will also be discussed.

**20.5 A COMBINED COMPUTATIONAL AND EXPERIMENTAL STUDY OF ION BEAM MODIFICATION OF CARBON NANOTUBES**

Boris Ni, University of Florida, Department of Materials Science and Engineering, Gainesville, FL; Rodney Andrews, David Jacques, Dali Qian, Center for Applied Energy Sciences, The University of Kentucky, Lexington, KY; Muthu Wijesundara, Yongjiao Yue, Luke Hanley, The University of Illinois at Chicago, Department of Chemistry, Chicago, IL; Susan B. Sottos, The University of Florida, Department of Materials Science and Engineering, Gainesville, FL.

The modification of bundled singlewalled and multiwalled carbon nanotubes are examined using a combination of computational and experimental methods. The computational approach is classical molecular dynamics based on the many-body reactive empirical bond-order potential parameterized by Brenner. The simulations consider the deposition of methyl ions on incident energies of 10, 45, and 80 eV. These predict the chemical functionalization of the nanotube surface, and formation of defects. As a result, the nanotube walls and the formation of cross-links between neighboring nanotubes or between the walls of a single nanotube. They also illustrate the manner in which the number of walls in the nanotube and incident energy affect the results. In general, multiwalled nanotubes with about 40 shells (average diameter of 25 nm) are synthesized by chemical vapor deposition. CF3+ ions are deposited at incident energies of 10 and 45 eV and then the nanotubes are examined with scanning electron microscopy and scanning electron microscopy. These experiments find strong evidence of chemical functionalization, in agreement with the simulation results.

**20.6 BAND FILLING AND CORRELATION EFFECTS IN ALKALI METAL DOPED CARBON NANOTUBES**

Jwoe Choi, Iran Amido Sampon, Louisiana State University, Center for Advanced Manufacturing and Physics, LA; Seong-Chul Lim, Jeju National University, Semiconductor Physics Research Center, KOREA; Young Chul Choi, Samsung SDI, Corporate R&D Center, KOREA; Chulku Jo, Young Hee Lee, Sungkyunkwan University, Dept of Physics, Korea; Paul A. Dowben, University of Nebraska-Lincoln, Dept. of Physics and Astronomy, NE.

We have investigated modification of the electronic structure of the vertically aligned multiwalled carbon nanotubes (MWCNTs) as a function of sodium doping. The changes in band structure can be largely associated with shifts of the Fermi level position relative to the multiwalled carbon nanotube band structure. The changes in the apparent density of states in the vicinity of the Fermi level suggest effects associated with the repulsive on-site Coulomb interaction (the correlation energy) although the intrinsic poor screening in the quasi-one-dimensional carbon nanotubes, particularly near the tube termination, cannot be neglected entirely. The results are compared with "unaligned" single walled and multiwalled carbon nanotube films (or mats).

**20.7 ATOMIC STUDY OF MECHANICAL PROPERTIES OF CARBON NANOTUBES**

T. Narita, K. Shintani, Univ of Electro-Communications, Dept of Mechanical Engineering and Intelligent Systems, Tokyo, JAPAN

The mechanical properties of single-walled carbon nanotubes are investigated by means of molecular dynamics simulations. The Tersoff-Brenner potential is used for the calculation of the interatomic forces. Two kinds of simulation cells are considered; one adopts the periodic boundary condition along the tube axis and the other corresponds to tube clusters. The atoms at the ends of a simulation cell are translated along its axis, and the Young’s modulus and Poisson’s ratio are estimated. How these mechanical properties of carbon nanotubes depend on their temperature and chiral vectors is discussed.

**20.8 CARBON NANOTUBES UNDER BENDING STRAIN**

M. Hakalainen, A. Rusanen, K. Kaski, Research Centre for Computational Engineering, Helsinki University of Technology, Helsinki, FINLAND

Carbon nanotubes are highly elastic semiconducting or metallic all-carbon molecules. Single walled nanotubes can be visualized as a graphitic layer rolled seamlessly into a tubular form. The tubes are considered to be an extremely promising novel material both for nanoelectronics and for structural properties based applications. From the new generations point of view no structure is perfect and defects, strain, and the resulting deformations play a significant role on the properties of a structure. This is especially true for carbon nanotubes, in which small changes in the structure can change the properties considerably. We study the effects of strain and strain induced defects and deformations by computer simulations. The structural effects are first looked into by employing a Molecular Dynamics scheme based on Brenner’s carbon potential energy model. For critical parts of the structure, Tight Binding calculations are then performed in order to obtain more precise information. Here we report the results on carbon nanotube junctions. Carbon nanotube junctions are considered to be one of the key structures in future applications because of the interface formed between the tubes of different conductivity. In this work we present the results of a comparative computational study of single walled carbon nanotube junctions in uniform carbon nanotubes under bending strain.

**20.9 FULLERENES INSIDE CARBON NANOTUBES: HOW LARGE CAN THEY BE?**

Miguel Horoz, LA. Gimbut, Dep. of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA.

The potential energies of interaction between carbon nanotubes and internal fullerenes of spherical and ellipsoidal shape, as well as between nanotubes in multi-walled nanotubes were calculated using
the Lennard-Jones potential for carbon-carbon interactions. The distribution of carbon atoms was assumed to be continuous on all considered structures. The optimal size of internal fullerenes and multi-walled nanotubes are determined as a function of the external nanotube radius. It was found that the potential energy minimum, the van der Waals distance is close to that in graphite for all studied cases. For the maximum size of internal fullerene, the van der Waals distance can be decreased by up to 0.8 Å, depending on the fullerene shape. The calculated results are in agreement with available experimental observations and can be used as a guide for future experiments.

20.10 MECHANICAL PROPERTIES OF STACKED LAMPSHADE NANO TUBE Takaya Hayashi, Morinobu Endo, Shinshu Univ. Dept. of Electrical and Electronic Engineering, Nagano, JAPAN; Humberto Terrones, IPICYT, San Luis Potosí, MEXICO

Stacked lamps shade nanotube is a different form of nanotube having sideways not parallel to the longitudinal tube axis, meaning that each layer has their edge exposed at the surface of the tube. Considering the structure, we can easily imagine that the mechanical properties can be completely different from the conventional nanotubes. Lambs shade tube might be weaker compared to the conventional tube on the tensile strength basis, but under the compressive stress, the stacked structure will act as a damping mechanism which could suppress the physical impact, vibrations and sonic waves when applied to composite material. In this presentation, we will deal with the study on mechanical properties of this nanotube via computational simulations, and the results of various modes of deformations, such as bend, stretch and twist will be presented.

20.11 PRESSURE ISOThERM OF HYDROGEN ABSORPTION IN CARBON NANOSTRUCTURES Xinhong Chen, Urumu Dettloff-Weglikowska, Mieko Hoshiki, Martin Hultman, Siegfried Roth, Max-Planck-Institut für Festkörperforschung, Stuttgart, GERMANY; Michael Hirsch, Marion Becker, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY

The hydrogen absorption capacity of various carbon nanostructures (single walled carbon nanotubes, activated carbons) is measured as a function of pressure (up to 80 bar) at different temperatures (7K, 200K, room temperature) using volumetric method. At room temperature and 80 bar the hydrogen storage capacity is less than 1 wt% for all samples investigated. The storage capacity depends roughly linear on hydrogen pressure. Upon cooling the hydrogen storage capacity increases and the best result of hydrogen absorption for single walled carbon nanotubes reaches about 2.7 wt% at 77K and 80 bar. The correlation between hydrogen storage capacity and surface area (BET) will be discussed.

20.12 ELECTROCHEMICAL INSERTION OF LITHIUM IN MULTI-WALLED CARBON NANOTUBE FILMS AND THEIR APPLICATION AS ANODE IN LITHIUM ION BATTERIES Hanjoon Jung, Lim Hyuck, Jong-Hyuk Park, Min Park, Byoung-Dong Kim, and Seung-Ki Joo, School of Materials Science and Engineering, Seoul National University, Seoul, KOREA

Vertically aligned multiwalled carbon nanotubes (CNT) films have been obtained by DC plasma-assisted hot filament chemical vapor deposition (CVD) over Ni/Cr/SiO₂. About 3 micrometer thick as grown film was electrochemically characterized for applications as sodium ion battery electrodes. Cyclic voltamograms of CNT/1 M LiClO₄/PC/Li half cell show that CNT films reversibly intercalate Li mainly under 0.7 V. Reversible capacity (1mA/cm²) has been estimated from galvanostatic charge-discharge characteristics under constant current density of 1mA/cm². Kinetic studies on the lithium intercalation reaction also have been carried out using electrochemical impedance spectroscopy (EIS). Reversible capacity was quantitatively analyzed using Electrochemical impedance spectroscopy (EIS). They employed 10 μm thick LiClO₄ screen printed on stainless steel mesh as cathode to characterize the full cell of CNT/LiClO₄/1 M LiClO₄/PC/CNT system, for the first time. Twenty charge-discharge cycles have been performed and, no noticeable performance degradation was found compared with LiClO₄/1 M LiClO₄/PC/Li cell.

20.13 Abstract Withdrawn.

20.14 Abstract Withdrawn.

20.15 NANODISK FIBERS FOR ELECTRODE WITH LARGE CAPACITANCE J.G. Wen, Y. Yu, W.Z. Li, J.H. Chen, and Z.F. Ren, Department of Physics, Boston College, Chestnut Hill, MA, USA

Due to the nanometer size, high surface area, good conductivity and chemical stability, carbon nanotubes are potentially superior electrode materials with large capacitance. Compared to nanotubes, the accessible surface area of nanodisks is much larger because of the large amount of dangling bonds at the edge of nanodisk fiber. Carbon nanodisk fibers have been directly grown on graphite foil as a binder-free electrode. Electrochemical characterization shows that this kind of carbon nanodisk electrode has several advantages: sufficient mechanical strength, binder-free, and minimum contact resistance between carbon nanodisks and the current collector. Transmission electron microscopic studies showed that surface structures of nanodisk fibers could be modified by annealing as-grown nanodisk fibers in air. The large accessible surface area was confirmed by the high specific capacitance and featureless rectangular-shaped cyclic voltammograms over a wide range of scan rates.

20.16 RAMAN INVESTIGATIONS OF H₂O, O₂, AND H₂O ABSORPTION IN NANOTUBES AND ACTIVATED CARBON Keith A. Williams, U.J. Kim, B.K. Pradhan, M.K. Kostov, M.W. Go, P.C. Ecklund, Pennsylvania State University, University Park, PA; T. Enoki, Tokyo Institute of Technology, Tokyo, JAPAN

We report Raman spectroscopic studies of H₂, H₂O, and O₂ adsorbed on single walled and carbon nanotubes and activated carbons at elevated temperatures and pressures. Shifts in the stretching mode frequencies of these adsorbates are correlated with the strength of the surface interactions. Also, the rotational spectra of these adsorbates are used to examine the effect of confinement within the nanotubes on the freezing transitions. This work was supported by NSF MRSEC (P.I. Burdett).


¹³C NMR studies were carried out in purified bundles of SWNTs. Degraded and purified SWNTs exhibit 2 groups of relaxation times: "fast" ~ 10 sec and "slow" ~ 40 sec. The origin of these different relaxation times is not clear, although they might be assigned to metallic and semiconducting tubes, as reported previously [1]. Admission of 0.2 g/m (1 atm at room temperature) to the system affects these relaxation times. The slow relaxation time decreases significantly, while the fast relaxation time is found to be only slightly changed. The data therefore suggest that the semiconducting tubes are involved in a weak chemisorption (weak charge transfer), whereas the metallic tubes are not. Also the effects to the effect of hydrogen on the relaxation times has been studied and will be reported. The NMR observations are supported by thermoelectric power and gravimetric studies on SWNTs under similar conditions

This work was supported by ONR (ONR N00014-96-1-0619).


20.18 CHEMICAL MODIFICATION OF SINGLE-WALL CARBON NANOTUBES USING MONOCHLOROBENZENE. Minfeng Zhang, Minsko Yudinitsky, Akira Koshio, ICBP, Japan Science and Technology Corporation, Tsukuba, JAPAN; Sumio Iijima, Meijo Univ., ICBP-JST, NEC, Tsukuba, JAPAN.

Our recent studies have shown that it is possible to modify single-wall carbon nanotubes (SWNTs) chemically by using monochlorobenzene (MCB) with ultrasonic treatment. We will describe their properties in this presentation. Themogravimetric analysis (TGA) results showed that the burning process of the modified SWNTs was separated into two or more steps, indicating that there are at least two types of the modified SWNTs. TEM images showed SWNTs were modified at their outside and inside-walls. Raman spectra of modified SWNTs had a new peak at about 1350 cm⁻¹, and their tangential mode shifted slightly to the higher energy side compared with the spectra of the original SWNTs. This reflects the MCB treatment changing the chemical structure of SWNTs and influencing their optical properties.

We analyzed the electrical resistance of the modified SWNTs from room temperature to 50 K. The resistance versus temperature of original purified SWNTs was parallel with a minimum at about 170 K, indicating that metallic behavior became semiconduct-like below 170 K. The resistance of the modified SWNTs increased as the temperature decreased, indicating that the modified SWNTs had the characteristics of a semiconductor. These results show that chemical
modification of SWNTs by MCB changed their structure and chemical and electrical properties.

**Z0.19**

**INFRARED SPECTROSCOPY STUDY OF PRISTINE AND FUNCTIONALIZED CARBON NANOTUBES.** Jean-Louis Buquettes, David Maurin, Jean-Louis Sauvajol, Groupe de Dynamique des Phases Condensées (UMR CNRS 5681), Université Montpellier II, Montpellier, FRANCE; C.L. Huiller, Françoise Beaune, Ecole Polytechnique, Palaiseau, FRANCE.

Resonant Raman scattering is widely used to study single-walled nanotubes (SWNT). On the other hand, experimental infrared studies remain very small or multiwall carbon nanotubes. Tangential and radial infrared modes are identified. The sensitivity of infrared transmission measurements is pointed out. The results are in good agreement with our calculations of active infrared modes. FTIR is one of the most powerful techniques to study organic fingerprints. Chemical processes and functionalization of SWNT lead to organic groups located at the surface of the tubes. On the basis of FTIR results obtained on pristine samples, we discuss here spectroscopic studies of functionalized samples modified by: (1) electrons produced by Van de Graaf accelerator, interaction with electrons leading to the presence of localized defects. (2) By chemical reactions with organic mixtures that induce various defects.

**Z0.20**

**DONOR-ACCEPTOR COMPLEXES OF CARBON NANOTUBES WITH ORGANIC CHLOROPHILES: EXPERIMENT AND THEORY.** Kristopher E. Wise, NRC/NASA/LSFC, Hampton, VA; Cheek Park, ICASE/NASA/LSFC, Hampton, VA.

The lack of an adequate method for manipulating and dispersing carbon nanotubes is a key obstacle to their widespread use in organic materials. Recent experimental work [1,2] suggests that carbon nanotubes form thermally stable intermolecular (noncovalent) complexes with certain conjugated organic molecules. These findings are significant because they provide a chemical handle for nanotubes that do not significantly perturb the extended pi-conjugative system. This property makes nanotubes useful for many of their impressive properties. This contribution describes a combined experimental and theoretical study aimed at understanding the nature of the interaction and identifying new complexes with improved properties.


**Z0.21**

**IN SITU CHEMICAL EXPERIMENTS IN CARBON NANOTUBES.** Nevin Nacib, Yuriy Gogotsi, Drexel Univ, Dept of Materials Engineering, Philadelphia, PA; Joseph Libera, Northwestern Univ, Dept of Materials Science and Engineering, Evanston, IL.

Nanotubes are considered for monolithic applications, such as drug delivery to a single cell or interconnects in nano-fluidic chips. We developed a new method for making nanotubes, which is hydrothermal synthesis, and Gogotsi, et al., J. Mater. Res., Vol. 15, No. 12, 2551-2558, 2000). Graphitic carbon nanotubes were synthesized in high temperature autoclaves by using an equilibrated C-H-O fluid. TEM and electron diffraction analysis show that these carbon nanotubes are characterized by high perfection of graphite layers, long and wide internal channels and internal liquid inclusions trapped during the synthesis. Hydrothermal nanotubes typically have 20-70 layers in their walls (wall thickness 7-25 nm) and an outer diameter of about 100 nm. Closed hydrothermal nanotubes, unlike conventional nanotubes produced in vacuum or at ambient pressure, contain water and gases encapsulated under pressure. During the growth, the synthesis fluid exists inside the tube. After closure of the tube, aqueous liquid and gases are trapped inside. H2O, CO and CH4 are expected to dominate from thermodynamic calculations. The liquid inclusions were studied by using TEM, where specific condensation and evaporation of liquid as well as a strong interaction between the liquid and the nanotube walls, including wall dissolution, were observed. These processes were studied for the first time in situ with the lattice fringe resolution. The presented work demonstrates the possibility of surface modification and chemical nanomodeling of nanotubes using entrapped aqueous fluids.

**Z0.22**

**Ferroelectric Actuation Mechanism in Carbon Nanotube Sheets.** Geoffrey M. Spinke, Gordon G. Wallace, University of Wollongong, Intelligent Polymer Research Institute, Wollongong, AUSTRALIA; Leonard S. Fifeild, Larry R. Dalton, University of Washington, Dept of Chemistry, Seattle, WA; Alberto Manzoli, Danilo De Rossi, University of Pisa, School of Engineering, Pisa, ITALY; Ilya I. Khayrutdinov, Roy E. Baughman, Honeywell Int., Honeywell Technology Center, Morristown, NJ.

A new mechanism for electromechanical actuation giving giant strains is demonstrated for sheets of carbon single-walled nanotubes (SWNTs) used as artificial muscles. An electrochemically reorganized network of self-assembled nanotube bundles provides microscopic gas pressure containers in which actuation is pneumatically driven. The carbon nanotube array acts as a strain amplifier, so a 3% actuator stroke in the in-plane direction is amplified to over 300% in the thickness direction. This thickness-direction actuation mechanism is ten times higher than previously reported for a low-voltage actuator material providing a fast response. Strain amplification results from Poisson’s ratio that is less than 0.2% times larger than for most solids. This Ferroelectric Actuation Mechanism (FAM), provides microscopic gas pressure containers for non-Ferroelectric actuators, associated shape memory and hydrogen storage effects, and a means for switching volume dependent properties.

**Z0.23**

Abstract Withdrawn.

**Z0.24**

**HIGH RESOLUTION MAGNETIC FORCE MICROSCOPY SUPERSTIPS PRODUCED BY FOCUSED ELECTRON BEAM INDUCED DEPOSITION.** L. Ulke, P. Hoffmann, Institute of Applied Optics, Department of Microtechnique, Swiss Federal Institute of Technology, Laussanne, SWITZERLAND; R. Berger, IBM SSD GmbH, Mainz, GERMANY; L. Scudellari, Nanosurf AG, Liestal.

Tip species of commercial pyramidal Si scanning probes were magnetically functionalized by means of focused electron beam (FEB) deposition. Induced deposition is experimentally shown for the first time that deposition can be directly related to the specific apex diameter. Using magnetic force microscopy, magnetic bit periods, magnetic particles and other magnetic structures can be resolved on storage hardisks. As precursor acetylacetonate Co(II)CO3 was used. The FEB deposition composition was determined by Auger Electron Spectroscopy. 14-26% % Co, 74-6% % C, and 10-12% % O depending on deposition parameters. With regard to the precursor stoichiometry 11% % O and 44% % Co, the composition in the deposit is lower (factor 1.3-2.5 for Co, 1.4 for C) whereas the oxygen content is lower (factor 0.2-0.64). The attempt to explain the product formation is carried out considering the electron beam assisted Co catalyzed thermodynamic equilibrium formation of the Boudouard reaction describing the equilibrium of the most probable carbon monoxide (CO) and the reaction products carbon (C) and carbon dioxide (CO2). The deposits show no aging or loss of functionality with storage time. The deposit nanostructure revealed by transmission electron microscopy consists of cobalt nanoparticles with a phase of 2-9nm in a carbon nanobeam dispersed in a polycrystalline matrix. Currently, FEB deposition experiments are being carried out to achieve the final resolution limit given by the monocrystalline size.

**Z0.25**

**NANOSENSOR DEVICES.** A.L. Minett, Media Lab Europe, Dublin, IRELAND; H.L. Shepherd, National Centre for Sensor Research, Dublin City University, Dublin, IRELAND; M. in het Panhuys, Media Lab Europe, Dublin, IRELAND.

Biological molecules and systems have a number of attributes that make them highly suitable for the development of sensing devices. Both macro- and to an increasing extent microscale biosensing devices have been extensively researched over the past decade.

Proteins fold into precisely defined shapes, nuclear acids assemble according to well-understood rules and antibodies and enzymes are highly specific in recognising their respective ligands. These attributes are governed by molecular behaviour at the nanoscale, where chemistry, physics, biology and informatics overlap. This presentation will highlight how the synthesis and self-assembly of nanosensors is now converging in nanotechnology. Although very promising, the bio-related aspects of nano-particles, -systems and devices are less developed than their non-biological cousins. This has become increasingly obvious that nano-devices exhibit peculiar behavior that is not necessarily predictable from that observed at macroscale level. Carbon nanotubes have been shown to exhibit unusual physical properties; hence it is our aim to devise a range of biological sensors on a nanoscale, using carbon nanotubes as the transducer in biosensor devices. Utilising a range of biological recognition entities (antibodies, enzymes or RNA), nanoscale sensory
systems can be made specific to a range of biological analyses of interest to the medical industry. For instance, to not only distinguish one cancer type from another but also to detect the very early stage of a mixture, such as glucose and protein levels in blood. Development of such devices on a small scale could lead to truly in-situ physiological sensing. For instance, sensory systems that detect physical interactions between diseases in the body could lead to a shift in focus of medical research from disease treatment towards earlier detection and prevention.

20.20
THE PREPARATION AND OPTIMIZATION OF CARBON NANOTUBE SHEETS FOR ELECTROCHEMICAL ACTUATOR APPLICATIONS

Methods are described for the preparation of carbon nanotube sheets having increased surface area and mechanical properties for electrochemical actuator applications. The processes exploit highly purified single-wall nanotubes, methods for debundling carbon nanotubes, processes for achieving sheet orientation, and mechanical homogenization to achieve suspensions with uniform aggregate size. Modulus increases of about an order of magnitude (to 7 GPa) resulted for nanotubes that had no preferred direction of orientation within the sheet plane. Partial tube orientation within the sheet plane was achieved both by post-fabrication and pre-fabrication processes (in a flow field during sheet formation). Since the actuator strain is independent of local level, the product of actuator strain [0.5%] and observed values of the modulus (50 MPa) can be used to calculate the maximum geometric work per cycle in the absence of creep. While this work per cycle (200 J/kg) is about three times higher than for hard ferromagnets, creep processes must be eliminated in order to make practical actuator devices.

20.27

The electronic and transport properties of single-walled carbon nanotubes (SWNT) have been shown to be sensitive to the presence of oxygen. At ambient temperature, large positive thermopower values, $V > 40 \mu V/K$, are observed in nanotubes when the tubes are oxidized. New experimental studies also reveal that, via oxygen doping, the thermopower can be reliably “tuned” to select intermediate values (between zero) between that found for a fully oxygenated and oxygen-depleted state.

This work was supported by ONR (ONR N00014-001-L-0019).

20.28
UTILIZING ANCIENT EGYPTIAN WISDOM FOR CONTROLLING THE INTERFACIAL BEHAVIOR OF CARBON NANOTUBES: Rajbinder Bandyopadhyaya, Elnat Nativ-Rot, Oren Negev, Rachel Yervish-Aizen-Rosen, Department of Chemical Engineering and The Ben-Zion Center for Meso and Nano Scale Science and Technology, The Ben-Gurion University of the Negev, Beer-Sheva, ISRAEL.

Single-Wall Nanotubes tend to pack into crystalline ropes that further aggregate into tangled networks, due to strong inter-tub-der van der Wals interaction. Aggregation acts as an obstacle to most applications, and attenuates the special properties of the individual tubes. We developed a simple procedure for dispersing PDDAMP produced nanotubes powder into individual, isolated tubes. A two-step process of dispersing in aqueous solutions of Gum Arabic, a natural polyelectrolyte, and re-dispersing leads to the formation of highly concentrated (up to 50%) stable, dispersion of isolated tubes. The method is inspired by the ancient Egyptian recipe used for preparation of carbon-black ink. The use of GA for stabilization of SWNT dispersions offers a few advantages: Disruption of the intertube interactions lead to dispersion enables the testing of isolated tube properties, and comparison to theoretical predictions. From the practical point of view, the ability to prepare a dry powder of isolated tubes, well separated by a polymer spacer, offers a biopharmaceuticals effect in pulling single tubes from an as-synthesized powder. The adsorbed polymer is expected to act as a compatibilizer leading to marked strengthening of the nanotube-matrix interface. We envisage that polymer-coated tubes will also find use for the production of “instant” nanotube powder, to be used in the field of reinforced elastomers and of nanoelectronics.

20.30
A STUDY IN THE DISPERSION OF CARBON NANOTUBES Matthew Brackler, Bonnie Gersten, Wendy Kosik, U.S. Army Research Laboratory, AMRL-WM-M, Aberdeen Proving Ground, MD; Helen Ji, Jimmy Mays, Department of Chemistry, University of Alabama, Birmingham, AL.

In the past, the dispersion of carbon nanotubes (CNTs) in both liquids and solids has been difficult due to the high surface interactions between the tubes. Dispersion of polymer CNT composites is important for such benefits as structural reinforcement of composites, the percolation threshold of CNT based conducting materials, and the thermal properties with the exploitation of the high surface area of CNTs. In this paper we discuss two approaches towards addressing dispersion of multivalled nanotubes (MWNTs). One approach is the use of surfactant chemicals selected on the basis that they interact with CNT chemical groups. The second approach is the functionalization through covalent bonding of the CNTs with various polymers including polystyreneimine (PEI), polyethylene oxide (PEO), and polydimethylacrylate (PDMA). The two approaches were evaluated to determine whether covalent functionalization was more beneficial than the use of surfactants. Characterization of the dispersion was performed using various microscopy techniques and surface analysis was performed using x-ray photoelectron spectroscopy (XPS).

20.31

The thermoelectric response of a mat of carbon nanotubes is shown to be sensitive to the detection of the molecule-SWNT interaction. In this presentation, we consider the effects of the vapor adsorption of a series of six-membered-ring hydrocarbon molecules with varying degrees of π electron population, heteroatoms (N), and adducts, etc. A wide variety of the thermoelectric response to these similar molecules is observed. For example, no response, or a complete reversal of the thermopower sign at 300 K is observed, depending on the structure of the adsorbed molecule. A heterogeneous model is proposed to explain the experimental data.

This work was supported by NSF MRSEC(PSU).

20.32
CARBON NANOSTRUCTURES PREPARED BY LASER ABLATION OF TRANSITION METAL-CONTAINING GRAPHITE IN OXYGEN ATMOSPHERE. K. Nakajima, T. Yamamoto, J. Tashiro, A. Smuki, M. Yoshimoto, Tokyo Inst. of Tech., Yokohama, JAPAN; P. Almeid, T. Chikyow, Nonmaterial Lab. COMET, Tsukuba, JAPAN; Y. Tokagi, Tokyo Univ. of Sci. Tech., Yamazaki, JAPAN.

Carbon nanostructures, such as C60 fullerenes, carbon nanotubes (CNTs) and carbon nanofoams are very promising materials for superconductors, scanning probes, hydrogen storage or field emitters. Growth of CNTs or carbon nanofoams reported are performed through arc discharge, chemical vapor deposition and laser ablation. method, usually through the metal catalyst. On the other hand, we recently have succeeded in growth of diamond films by laser ablation of pure graphite target in an oxygen atmosphere, and diamond crystals are grown epitaxially on single-crystal aluminium oxide (sapphire) substrates, Nature, vol 399 (1999) 306. In our latest publication, films, diamond films are grown in oxygen atmosphere and grown on the substrate which is placed parallel to the target and about 3cm away from the target surface. In this experiment, we employed the laser ablation of transition metal-containing graphite for synthesis of carbon nanofoams. Resultant carbon materials were characterized by FESEM, TEM, XRD and Raman Scattering Spectroscopy. By using a graphite target containing the transition metal oxide such as NiO or Fe$_2$O$_3$, highly oriented carbon nanofoams of 10-30nm in diameter were grown toward the target from the substrate surface. During the depositions, the oxygen pressure was kept at 50-200 mTorr, and the substrate was heated at 370-1070°C. Nanofoams could be grown at temperatures above 500°C, and diameter of nanofoams increased as the substrate temperature. The relationship between the structures of these nanofoams and the laser ablation parameters are discussed in this talk.
Carbon single-wall nanotubes (SWNTs) are capable of adsorbing hydrogen at room temperatures and pressures [1-4]. Although early experiments were performed on highly impure samples, hydrogen storage densities were estimated to be between 5 and 10 wt% on a SWNT weight basis. Since that time we have developed methods for obtaining SWNTs in purities as high as 98 wt% [5], and developed methods to activate these materials for hydrogen storage. The activation process involves exposing the pure SWNTs to high-intensity ultrasonic energy, which cuts the tubes into shorter lengths. An impurity metal alloy is also introduced into the SWNTs during this process. Detailed analysis, performed with carefully calibrated equipment shows that the SWNT fraction of the composite material can adsorb up to 7 wt% hydrogen. The role of the impurity metal alloy introduced during processing will be discussed. Two-color Ramanscattering spectroscopy shows that this variation in material synthesis can lead to the formation of tube samples of differing chirality. Adsorption measurements on these samples reveal a link between SWNT chirality and hydrogen capacity. This data will be discussed with respect to the mechanism of hydrogen desorption and the relationship between electronic and structural factors.


9:30 AM #210.3


We report [6 wt%] storage of H2 at T=77 K in aggressively processed bundles of single-walled carbon nanotubes at p=2 atmospheres. The hydrogen storage isomers are completely reversible. We confirm the high storage values for H2 and further reveal the effects of quantum mechanical zero point motion. We propose that the post-synthesis treatment of the sample not only improves access of the hydrogen to the central pore within an individual nanotube, but also may create a roughened tube surface (via S-T wall defects) with an enhanced binding energy for hydrogen. This enhancement is needed to understand the strong adsorption at low pressure. We obtained an experimental value for the isosteric of 130 mJ/eV near liquid N2 temperature.

9:45 AM #210.4


In situ resistivity ($\rho$) and thermoelectric power (S) have been used to study the nature of the adsorption of hydrogen into bundles of single-walled carbon nanotubes (SWNT) for pressures p < 1 atm and temperatures T=77 K<T<500 K. Isothermal plots of S vs. 1/\rho are found to exhibit linear behavior as a function of gas coverage, consistent with a physisorption process. Studies of S, $\rho$ at T=500 K as a function of pressure exhibit a plateau at a pressure p ~ 30 Torr, the same pressure where the H2 wt% measurements suggest the highest binding energy sites are being saturated. The data have been interpreted to indicate that H2 is physisorbed in SWNTs for p < 1 atm and T > 500 K.

This work was supported by HONDA R&D.

10:30 AM #210.5

CARBON NANOTUBE ANODES FOR LITHIUM ION BATTERIES: Ryne R. Raffaele, Thomas Gennett, Laboratory for Micropower Research, Rochester Institute of Technology, Rochester, NY; Jeff Murdick, Prashant Khunti, Carnegie Mellon University, Pittsburgh, PA; Alexander F. Hepp, NASA Glenn Research Center, Cleveland, OH; Michael J. Heben, Anne C. Diller, Kim C. Jones, National Renewable Energy Laboratory, Golden, CO.

This presentation outlines the evaluation of carbon nanotubes for use in thin film lithium ion batteries. Highly purified single-wall carbon nanotubes (SWNT) were obtained through chemical refinement of soot generated by pulsed laser ablation. The purity of the nanotubes was determined via thermogravimetric analysis, two wavelength Raman spectroscopy, and transmission electron microscopy. Electrical measurements, the specific surface area and lithium capacity of the SWNTs were...
microscopy, field emission devices, nanoelectronics, H2 storage, electromagnetic absorbers, ESD, EFM films and coatings and structural composites. Functionalized and purified CNTs are compatible with many host polymers are needed. A novel microwave CVD processing technique to meet these requirements has been developed at Penn State Center for the Engineering of Electronic and Acoustic Materials and Devices (CEEAM). This method enables the production of highly purified carbon nanotubes with variable size (from 5-40 nm) at low cost (per gram) and high yield. Whereas, carbon nanotube synthesized using the laser ablation or arc discharge method is not purify due to catalyst or catalyst support. The Penn State research is based on the use of solvents over other metal/metal oxides in the microwave field for a high production and uniformity of the product. An extended conventional purification method has been employed to purify our products in order to remove low contami. A novel composite structure can be tailored by functionalizing carbon nanotubes and chemically bonding them with the polymer matrix e.g. block or graft copolymer, or even cross-linked copolymer, to impart exceptional structural, electronic and surface properties. Bio- and Mechanical-MEMS devices derived from this hybrid composites will be presented.

11:45 AM Z10.0
CHEMICAL FUNCTIONALIZATION OF CARBON NANOTUBES. Rodney Andrews, David N. Jacobs, Center for Applied Energy Research and Advanced Carbon Materials Center, University of Kentucky, Lexington, KY; John Anthony, Robert G. Bergosh, Monica Ho, Chad Lamdi, Fisan McKenzie, Mark S. Meyer, Grant J. Palmer, John P. Selegue, Department of Chemistry and Advanced Carbon Materials Center, University of Kentucky, Lexington, KY; Eric Grulke, Monica Karrandagull, Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY; Robert C. Hadron, Hui Hu, Department of Chemistry, University of California, Advanced Carbon Materials Center, University of Kentucky, Lexington, KY.

We have chemically modified SWNTs and MWNTs with a variety of different reagents to produce halogenated, alkylated, and otherwise modified nanotubes. The resulting nanotubes have been characterized by techniques that include FTIR, NAA, and SEM. In this talk we will report the types of chemical changes that have been induced in the nanotubes.

SESSION Z11: NANO-MODELED BASED DEVICES

Chair: Pulickel M Ajayan and Yuhshii Saxo

Thursday Afternoon, November 29, 2001

1:30 PM Z11.11
NANOENGINEERING OF CARBON NANOTUBES AND THE STATUS OF ITS APPLICATIONS. Yoshikazu Nakamura, Seiji Akitu, Osaka Prefecture Univ, Dept of Physics & Electronics, Osaka, JAPAN; Takashi Okawa, Daiken Chemical Co. Ltd, Osaka, JAPAN; Sigemori Yamazaki, Unizoku Co. Ltd, Osaka, JAPAN; Toshikazu Nosaka, Technology Research Institute of Osaka Prefecture, Osaka, JAPAN.

Recently, we have developed a well-controlled method for manipulating carbon nanotubes. The first crucial process involved is to prepare a nanotube array, named nanotube cartridge. We have found the ac electroplating of nanotubes by which nanotubes are aligned at the knife-edge. The nanotubes used were multiwalled and prepared by an arc discharge with a relatively high gas temperature. The second important process is to transfer a nanotube from the nanotube cartridge onto a substrate in a scanning electron microscope. Using this method, we have developed nanotube tips and nanotube tweezers that operate in a scanning probe microscope. For the nanotube tips, the advantage of their high aspect ratio has been revealed by imaging the 1-micrometre pitch line-and-space patterned on a Si wafer, its pits in 2D media, the local solution shell in water and the bio-cells such as human erythrocytes and proteins. Their high resolution has been confirmed for imaging DNA and a Si (111) 7 x 7 surface. The cyclic observation of the surface roughness of Si wafer has proved the nanotube tips to have longer lifetime than conventional Si tips. The nanotube tips have also successfully been applied to magnetic force microscopy. Kebire in force microscopy, micromachining and nanolithography. For the nanotube tweezers, two nanotubes were attached parallel to each other on the metal electrodes patterned on a conventional Si tip and its fixation were made by carbon deposition. The application of a dc voltage to the two nanotubes narrows the spacing between the tips of the nanotubes and it is fully closed when the applied voltage is beyond a certain value (pull-in voltage) which is less than 10 V. Furthermore, returning the applied voltage to zero opens it fully. Utilizing these nanotweezers, a scanning probe microscope has been developed that enables size-sensitive substances to be carried.
2:00 PM Z11.2
CARBON NANOTUBE 3PM PROBES: FUNDAMENTALS AND APPLICATIONS
Liwei Chen, Chih-Chung Chen, Kai Salhaueter, Gregory Verdi, Charles M. Lieber
Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA.

The contrast of SPM is based on the interactions between the surface and probe; therefore, the resolution of SPM imaging greatly depends on the geometrical and mechanical properties of the probes. Carbon nanotubes make potentially ideal tips for SPM due to their small diameter, high aspect ratio, mechanical robustness, electrical conductance and chemical functionality at the open end. Here we report the preparation of carbon nanotube probes by individual assembly or direct chemical vapor deposition. The fundamental resolution of such nanotube probes was investigated. The nanotube probes showed complex tip-induced broadening behavior in AFM imaging depending on the interaction between the probe and the surface. When imaging soft biomolecules in fluid, the resolution of these nanotube tips could be improved on the nanoscale level. As an example of the applications, nanotube probes were utilized in high-resolution imaging to study the structure of DNA repair glycoclypsine hOGG1. The reaction is biologically crucial in DNA repair and is suited for conventional structural method. Single molecule imaging of hOGG1-DNA complexes in air with carbon nanotube probes revealed drastic kinks at non-damaged DNA sites, which were previously believed to be induced by the protein only at damaged bases. These results suggest that hOGG1 causes substantial structural rearrangements in DNA while searching for damaged bases and a two intermediate mechanism by which hOGG1 searches for damaged bases in the genome was proposed.

2:15 PM Z11.3
IMPROVED RESOLUTION IN MAGNETIC FORCE MICROSCOPY WITH CARBON NANOTUBE TIPS
Peter Zefran, Dan Dabber, Univ. of Minnesota, MN; Katerina Moloni, Micradyne, Largo, FL; PioZIOMAX Technologies, Middleton, WI

Carbon nanotube Magnetic Force Microscopy (MFM) tips have been fabricated using commercially available silicon probes and bundles of or single multlwalled carbon nanotubes. These tips have been directionally coated with Cr/Co multilayers to produce either an effective magnetic contrast or magnetic dipole contrast, to the imaging measure of the sample's stray fields. Ex situ transmission electron microscopy was used to characterize the carbon nanotubes and these multilayer coatings. MFM images were acquired using a Digital Instruments Dimension 3100 in intermittent tapping mode. A comparison between our monolayer/dipole carbon nanotube MFM tips and commercially available MFM tips has been made using test tracks written into a perpendicular recording media with a bit transition period of 130 nm (330 KFCI). These carbon nanotube tips demonstrate exceptional durability while achieving resolution improvements of a factor of 3 over conventional MFM techniques.

3:00 PM Z11.4
THERMAL AND ELECTRONIC PROPERTIES OF A CARBON NANOTUBE-EPoxy COMPOSITE

We exploit the high thermal conductivity of single-wall carbon nanotube [SNTs] to augment the thermal transport properties of a widely used industrial epoxy. Preliminary results show significant enhancement of the composite thermal conductivity at all temperatures with low weight percent nanotube loading. Samples loaded with 1.0% SNT material show a temperature independent increase in thermal conductivity of nearly 50%, providing evidence that thermal conductivity is largely limited by tube-tube interactions. Electrical conductivity measurements provide evidence for the onset of a percolation effect between 0.2 and 0.56% loading, indicated by increases in conductivity of approximately four orders of magnitude. Results from samples of higher loading, various production techniques and samples incorporating different SNT materials will be presented.

3:15 PM Z11.5
ENERGY DISSIPATION IN CURRENT-CARRYING CARBON NANOTUBES
Philip Kim, Paul L. McElroy, Dept. of Physics, Univ. of California, Berkeley, CA; Li Shi, Arun Majumdar, Dept. of Mechanical Engineering, Univ. of California, Berkeley, CA.

The temperature distributions in electrically heated multi-walled nanotube [MWNT], metallic, and semiconducting single-walled nanotube [SWNT] have been measured in a transmission electron microscope. The temperature profiles along the tube axis in MWNT and semiconducting SWNT indicate the bulk dissipation of electronic energy to phonons, which suggests diffusive electronic transport. At low temperature, metallic SWNT exhibit non-dissipative transport, but dissipation can dominate the contacts between the tubes and the electrodes, while bulk dissipation has been observed at high bias voltages. This change from non-dissipative to dissipative, in metallic SWNT suggests that the electron transport in these nanotubes is ballistic at a low electrical field regime and it becomes dissipative at a high field regime, possibly due to optical phonon coupling.

3:30 PM Z11.6
DESIGN AND QUANTIFICATION OF A NANO SCALE FIELD EFFECT TRANSISTOR: MODE IN HASP LASIC, Media Lab Europe, Dublin, IRELAND; Jonathan Coleman, Department of Physics, Trinity College, Dublin, IRELAND; Brian Foley, Department of Electronic and Electrical Engineering, Trinity College, Dublin, IRELAND; Paul Popelier, Robert Mann, Department of Chemistry, UMIST, Manchester, UNITED KINGDOM; Werner Blau, Department of Physics, Trinity College, Dublin, IRELAND.

A new design for a field effect transistor able to push back the physical limits of Moore’s Law is described. The ON state of the device is characterized using a simple computer simulation. An electron introduced on one side of a conjugated molecular switching element can move across to the other side of a molecule in an electric field in the absence of a gate voltage, a process analogous to conduction. The presence of a gate voltage effectively interrupts conduction and suppresses conduction. A molecular-based processor of this type could demonstrate transistor density of up to 2 x 10^{12} transistors per cm^{2} and run at up to 12 THz.

3:45 PM Z11.7
CARBON NANOTUBE LOGIC GATES
V. Derycke, R. Jha, J. Appenzeller, Ph. Avouris, IBM T.J. Watson Research Center, Yorktown Heights, NY.

Single carbon nanotubes can be used as the active channel in field effect transistors (FETs). Without any special treatment, the obtained FETs are always P-type: the current carriers are holes and the devices are off for positive gate bias. Here we show that this transistor behavior is due to the pinning of the Fermi level at the valence band of the semiconductor substrate and the presence of a large Schottky barrier for electron injection into the device. The fabrication of N-type FETs has recently been achieved by doping the device with an electron donor such as potassium. We introduce a novel approach of converting SWNT-based P-FETs into N-FETs without the use of dopants. The technique relies on the control of the electrostatic barriers and the modification of the contacts. In this way, we can position the Fermi level at any position within the band gap in a controlled manner and therefore modify the character of the device. When the Fermi level lies in the middle of the band gap, the device shows both hole and electron conduction at negative and positive gate biases respectively. When the Fermi level lies close to the conduction band edge, the resulting FET is fully N-type. Using our technique, we are able to fabricate the first nanotube-based integrated logic circuit, a NOT gate (voltage inverter). Inverters using K-doped tubes were also fabricated. We will compare the voltage inverters made by the two techniques.

4:00 PM Z11.8
CONTROLLED CREATION OF A CARBON NANOTUBE DIODE BY A SCANNED GATE
Marcus Pecking and A.T. Johnson, University of Pennsylvania, Department of Physics and Astronomy, Philadelphia, PA.

We use Scanning Gate Microscopy to precisely locate the gating response in field-effect transistors made of individual semiconducting single wall carbon nanotubes. In all samples, a dramatic increase in transport current occurs when the device is electronically doped with holes near the positively biased edge of the Fermi level. This behavior with the turning on of a reverse biased Schottky barrier located at the interface between the p-doped nanostructure and the metal contact. By positioning the gate near one of the contacts, we induce rectifying behavior in the previously symmetric device. These experiments indicate a strategy for diode fabrication based on controlled placement of acceptor impurities near a contact.
nearly in the same direction confined by the shape and size of the
channels (2). Pyrolysis of organometallic precursor such as nickelocene
along with thiophene has also been reported to result in "Y"-shaped
junctions with angles between the arms vary in the range of 90° -
150° from junction to junction (3). Single wall Y-junctions have also
been observed by scanning tunneling microscopy in the residue of the
thermally decomposed C60 in the presence of transition metals (4).
For electronic property measurement and practical application, large
amount of high quality and identical-structured Y-junctions are
required. We have successfully synthesized the very straight carbon
nanotube Y-junctions by pyrolysis of methane over cobalt supported
on magnesium oxide. The Y-junctions have nice smooth surfaces and
uniform diameters, and the angles between the three arms are close to
120°. The Y-junctions carbon nanotubes grow in a similar way which
is very important in the development of nanoelectronic devices. With
the straight truly Y-junctions, the structure characterization and
electronic property measurement are going to be reported.

4:30 P.M. 211.10
AFM-BASED SURFACE POTENTIAL MEASUREMENTS ON
CARBON NANOTUBES. Sandra B. Schajman, Dept. of Physics,
Applied Physics and Astronomy, Robert Vajtai, Dept. of Materials
Science and Engineering, Yuriy Shusterman, Sujit Biswas, Brian
Dewhurst, Leo J. Schowalter, Dept. of Physics, Applied Physics and
 Astronomy, P. Ajayan, Dept. of Materials Science and Engineering,
Rensselaer Polytechnic Institute, Troy, NY.

In order to build electrical devices based on carbon nanotubes, it is
crucial to understand the effects of the substrate, electrical contacts,
defects and junctions on the transport properties of both multi-wall
and single-wall nanotubes (MWNT and SWNT). In the present study,
carbon nanotubes were deposited onto an insulating oxide layer over a
conducting substrate and platinum electrical contacts were prepared
via a Focused Ion Beam (FIB) deposition method. To investigate
transport properties, we used an atomic force microscope (AFM) to
determine the surface potential of MWNT. The technique employed
applies a dc-voltage to the tip that equilibrates the local electrostatic
potential on the sample so as to eliminate forces on the AFM tip
carried by electric repulsion or attraction between tip and sample. The
advantage of this method compared to other AFM-based techniques
to measure electrical properties is that there is no alteration of the
sample potential caused by the tip. An ohmic contact to the substrate
allowed us to polarize it at a different potential than the nanotubes
themselves. Surface potential measurements show that the potential
drops along the MWNT with a slope that varies with the bias applied
across the nanotube but also that slope changes near the electrical
contacts. With this method, we are also able to determine
configurations of charges trapped on the substrate near the nanotubes
and contacts, and their effect on the electrical properties of the
nanotubes. We will present results of measurements for different bias
configurations of both nanotubes, nanotube networks and substrates.