SYMPOSIUM W
Nanotubes, Fullerenes, Nanostructured and Disordered Carbon
April 17 – 20, 2001

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*Invited paper
SESSION W1: FULLERENES

8:30 AM W1.1
CRYSTALLOGRAPHIC STUDIES OF ENDONUCLEAR FULLERENES, FULLERENEPORPHYRIN Co-CRYSTALS AND FULLERENE DIMERS. Alisa B. Smith, Marilyn M. Olmstead, and D. E. Luzzi, University of California, at Los Angeles, CA; and David B. Goodgame, and David E. Luzzi, University of New Hampshire, Chemical Department, Durham, NH.

Recent advances in obtaining ordered crystalline forms of various fullerenes (including endonuclear fullerenes such as $\text{C}_{82} \text{OC}_{6}$, fullerene/porphyrin aggregates, and covalent complexes) have allowed us to obtain their structures through single-crystal X-ray diffraction studies. For related studies see: S. Stevenson et al. Nature 1999, 401, 55; M. M. Olmstead et al. J. Am. Chem. Soc. 1999, 121, 7000. This talk will present recent structural work in this area.

9:00 AM W1.2
PUTTING FULLERENES AND METALLOFULLERENES INTO CARBON NANOTUBES. Toshiki Tanaka, Nagoya University, Chemical Department, Nagoya, Japan; Katsutomo Suenaga, Kazuhiro Hirasaka, Shunji Bandow, and S. M. Iijima, Japan Science and Technology Corporation, Ibarak, Japan; and H. Shigematsu, Nagoya University, Chemical Department, Nagoya, Japan.

We report the high-yield synthesis for various empty fullerenes ($\text{C}_{60}$, $\text{C}_{70}$) and endohedral Ge, Sc, Sm metallofullerenes containing SWNTs through the vapor phase reaction and the spectroscopic characterization of the encapsulated metal atom ion by using the electronic energy-loss spectroscopy (EELS). For example, the obtained EELS spectra reveal that the encapsulated Sm ion takes 2 states in (Sm$_x$C$_{62}$) in SWNTs irrespective of the physical and the electronic properties of SWNTs. During the electron beam irradiation, the diamagnetic Sm$^{2+}$ spectrum is gradually converted to that of the trivalent Sm$^{3+}$. At the same time scale, the concentration of the Sm$_x$C$_{62}$ molecules within the SWNTs is observed by the high-resolution electron microscopy (HRTEM).

9:30 AM W1.3

The future application of single-wall carbon nanotubes (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 their lumens. This is potentially more robust than doping of external interstices of tubular bundles, for example. We have encapsulated a number of fullerenes inside SWNTs including C$_{60}$ as well as other higher order fullerenes and metallofullerenes such as La$_2$C$_{22}$ and La$_3$C$_{32}$. The structural properties of these nanotubocapsular hybrid materials have been studied using high resolution transmission electron microscopy and electron diffraction. It is found that the encapsulated fullerenes self-assemble into long, one-dimensional chains. Variation in ordering and coherence lengths among the chains of different species is evident in their diffraction signatures. In some cases, a sharp diffraction signature is produced, allowing a quantitative analysis of the 1D structure of the chain. In other cases, no signature is seen that can be assigned to the encapsulated molecules. Several interesting observations indicate that the surrounding nanotubes can have a profound effect on the stability and chemistry of encapsulated molecules. For example, some of the encapsulated fullerene molecules remain stable at temperatures above the point at which they would decompose under unconfined conditions. At temperatures which chemical reactions such as molecular coalescence occur, the nanotube can act to catalyze the reaction while templating the final product through steric confinement. Finally, the inherent mechanical stability of the SWNTs used in this study make these structures ideal for the study of the structure of single molecules. Using such observations, it is shown that the structure of C$_{60}$ is consistent with the electron structure of $\text{La}^{3+}$ and $\text{C}_6\text{O}^{2-}$ in comparison to ab initio calculations. The effect of encapsulation of such charge transfer molecules on the electronic structure of the carbon nanotube will be discussed.

10:45 AM W1.6
CLUSTERS SELF-ASSEMBLY IN ONE-BEAM OPTICAL TRAP. Eugene Collins, Don Henderson, Weihe Lu, Andrey Zvezdin, Fisk University, Physics Department, Nashville, TN.

Assembling of nano- and microstructures under presence of strong gradient optical fields, producing optical potential well, open new possibilities for control and fundamental understanding of the system synthesis. Last decade one-beam optical trapping influenced mostly to the microtechnology techniques. Contribution of optical trapping to nano-technologies promise to be more significant. Previous experiments in optical trapping showed trapped particles creating quantum-molecular symmetric structures, assembled together by photons and existing only in presence of laser field. Under the certain conditions photon C$_{60}$C$_{60}$ is converted to the chemical bonding. Thus assembled structures are stable without laser trap and can be used as elements of carbon-based devices. In our experiments one-beam optical trap was created by CW YAG laser radiation in 50 um-optical cell, filled by C$_{60}$/solvent solution. C$_{60}$ clusters were created on the glass surface and in the volume of solution, maximum up to 20 um size. It was possible to move the trapable clusters of different shape (lines, rods etc.) by motion of optical trap along surface of substrate and x-axis of laser beam. Parameters of photon and chemical bonding were measured during process of growth by spectrophotometry in laser trap. C$_{60}$C$_{60}$ bond shift in transmission spectra or by microscope w/CCD camera. After structure became stable and chemical bonding was created, AFM was used for surface scan. In our experiment spectral and AFM-images are presented and path of transition from photon bonding to chemical bonding are discussed.

11:00 AM W1.7
TRANSITION TEMPERATURE, CELL VOLUME AND ORIENTATION ORDER IN FULLERIDE SUPERCONDUCTORS - THE SEARCH FOR EXPANDED P433 SYMMETRY PHASES. P. Dorrad, M.J. Rosowsky, Univ of Liverpool, Dept of Chemistry, Liverpool, United Kingdom, and M. Y. Dubitsky, A. Znqo, Firelli Cesare Sistemi, Milan, Italy.
The transition temperatures of the $\alpha_2\beta_2$ superconductors increase with increasing pressure. The rate of increase depends strongly on the mode of interlayer ordering, with a much more pronounced dependence in the PdI$_2$ structure than in the other phases, which is the PdII structure of $\alpha_2\beta_2$. The dependence of higher $T_c$ in this family requires the preparation of examples with larger lattice parameters, which have been investigated for the substitution of potassium for sodium on the tetrahedral site. We will present structural, magnetic, and electronic data from these expanded and other $\alpha_2\beta_2$ phases (11.1.1). The potassium substitution produces the desired increase in lattice parameter, but suppresses $T_c$ below the values expected by extrapolation from the pure sodium PdI$_2$.

11:15 AM W1.8
STUDIES OF INDIGO-FULLERENES AND DOPED BUCKY ONIONS AS SEED MATERIALS FOR SOLID STATE QUANTUM COMPUTERS. Seongjun Park, Stanford University, Dept of Chemical Engineering, Stanford, CA, Deepak Srivastava, NASA Ames Research Center, Nanotechnology at CSS/JNAS, Moffett Field, CA, Yeehyung Cho, Stanford University, Dept of Mechanical Engineering, Stanford, CA.

Quantum computers potentially can exceed the computational efficiency of present day classical computers for certain classes of numerical problems. Experimentally, the progress is mostly achieved, in quantum computation, through bulk spin-resonance method via NMR on bulk liquids. [1] The measurable signal, however, decays according to the finite lifetime of coherence and the approach is not scalable to more than 10 qubit systems. As an alternative "solid-state" approach, we have proposed in arrays of suitable dopants, with 1/2 nuclear spin, with a requirement which is to be achieved from detailed nuclear spin/phonon point of view. Recently, we have proposed a nuclear magnetic resonance based approach for the encapsulation of a spin 1/2 dopant in a fullerenic matrix, which has been calculated as an alternative to the solid-state quantum computer application. [2] So, we have proposed a general microwave technique using 181 total energy pseudo-potential DFT based method. Total energy minimization of $^{13}$C and $^{35}$P in C$_{60}$H$_{2}$, C$_{70}$, C$_{80}$ and compressed bucky onion reveals a consistent behavior in the same materials in the C atom of the encapsulating matrix. The wall barriers for the encapsulation and escape have been calculated to facilitate the life times, and will be discussed for the suitability in a solid-state quantum computer application.

11:30 AM W1.9
THE INTERACTION OF C$_{60}$ WITH AMORPHOUS SILICON: TWO AND THREE DIMENSIONAL STRUCTURES. P. Reineke, P. Oelhafen, Universität BAS, Institut für Physik, Basel, SWITZERLAND.

In the present investigation we analyze the interaction between C$_{60}$ and silicon in two (layered) and three dimensional geometries: C$_{60}$ on an amorphous silicon (a-Si) layer, a-Si as top layer on a C$_{60}$ film, and C$_{60}$ incorporated in an a-Si matrix. The latter experiment makes use of the fullerene as a prefabricated, wide-bandgap structural unit embedded in a semiconducting matrix. The electronic structure and chemical bonding are observed with photoelectron spectroscopy in the ultraviolet (UPS) and X-ray regime (XPS), and Raman spectroscopy. The deposition is in all cases performed in-situ under ultrahigh vacuum conditions and incorporation of various amounts of C$_{60}$ in the a-Si matrix is achieved by co-deposition of the two components. At ambient temperature the C$_{60}$ molecule does not chemically react with Si and the matrix itself by the silicon matrix retains its basic electronic and chemical properties of the interface (band bending and offset) between silicon and C$_{60}$ in the layered, two dimensional structures are compared to the characteristics of the three dimensional arrangement. The behavior of C$_{60}$ in the a-Si/substrate (11.4.1.2). The depositions are discussed in view of the photocurrent process, core hole relaxation and barrier heights between the matrix and individual clusters. The potential use of C$_{60}$ as, firstly, quantum dot-like components and, secondly, materials with large inner surfaces can now be addressed.
200-nm pulses, total length 200 μ, 1.06 μm); and 3) cw CO2-LV at room temperature (10.6 μm). Raw material collected from different locations in the specimen (indicated by the in situ diagnosis) was characterized by Raman spectroscopy, TEM, and FESEM, and thermogravimetric analysis (before and after various chemical etches and oxidative purification treatments) to investigate the SWNT growth mechanism and to optimize the processing conditions for application of the SWNT in electronic devices. This research was supported by the U.S. Department of Energy and the Laboratory Directed Research and Development Program at ORNL under DE-AC05-00OR22725, with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

2:30 P.M. W2.3

PERFECTLY ALIGNED SINGLE WALL CARBON NANOTUBE CRYSTALS. Jin Won Seo, 1, 2, James K. Gimzewski, 3, Reo R. Schlicher, 4 Institute de Physique, Université de Neuchâtel, Neuchâtel, SWITZERLAND. 2 IBM Research Division, Zurich Research Laboratory, Zurich, SWITZERLAND. 3 Mark E. Welland, Engineering Department, University of Cambridge, Cambridge, UNITED KINGDOM.

Since the discovery of carbon nanotubes in 1991, 1 new methods of synthesizing multi-walled and single-walled carbon nanotubes (MWCNTs and SWCNTs respectively) have been developed from the initial use of electric arc discharges, to laser ablation and more recently catalytic chemical vapor deposition and solid-state chemical reactions. SWCNTs are currently the subject of much research because they represent an ideal 1-D nanostructure with unique physical properties. Nevertheless, only limited success has been achieved in the preparation of ordered bundles 2,3, which are thought to be held together by weak Van der Waals forces. Here we demonstrate a new breakthrough where perfect single carbon crystals made of well-ordered SWCNT bundles are directly fabricated using a nano-pattern formation reaction in vacuum transmission electron microscopy (TEM). Atomic Force Microscopy and Electron Energy Loss Spectroscopy were used to characterize the structure and unique ordering of these tubes. Single walled tubes within a single crystal were found to be completely straight and have uniform diameters of approximately 1.5 nm, which provides them with the unique capability to order in the micron scale. The bundles were found to terminate abruptly and they exhibit faceting, particularly in larger crystals.

References:


2:45 P.M. W2.4

THE TUBE-TUBE INTERACTIONS, GAS EXPOSURE AND ALCALI-METAL INTERCALATION IN SWNT BUNDLES STUDIED BY NUCLEAR MAGNETIC RESONANCE. Xiaoping Huang, Tideo Shimoda, Alfred Kleinhammes, Les Fleming, Re-Gao, Otto Zhao, Yue Wu, Dept of Physics and Astronomy, Univ of North Carolina, Chapel Hill, NC.

The 13C nuclear magnetic resonance technique has been successfully used to measure the quantities of carbon in the elementary density units at the Fermi level of the metallic tubes in single-walled carbon nanotube (SWNT) bundles (X. P. Tang, et al., Science Vol. 288, 492 [2000]). In the present work, we measured the magnetic field independence and linear temperature dependence of the 13C nuclear spin-lattice relaxation rate of the semiconducting tubes. It indicates a weak metallic behavior of the 'semiconducting' tubes in SWNT bundles and infers the tube-tube interactions. At one atmosphere pressure and room temperature, it was observed that the 13C nuclear spin-lattice relaxation rate is significantly affected by the exposure of the SWNT bundles helium gas but other inert gas. Our study also found that the intercalation of alkali metals into SWNT bundles substantially changes the electronic structure of the tubes in the SWNT bundles.

3:00 P.M. W2.5

CARBON AND CARBON-NITRIDE NANOTUBES. A. Zettl, Dept. of Physics, University of California at Berkeley, Berkeley, CA.

I will discuss some recent work on the structural, electrical, and mechanical properties of carbon and boron nitride nanotubes.

4:00 P.M. W2.6

NUCLEATION AND GROWTH OF CARBON CONES FROM MONOCLINIC CARBON RINGS. M.J. Stacey and J. Kilbourn, NEC Research Institute, Inc., NJ.

It is known that nested carbon cone structures can be generated by the partial pyrolysis of methane. In agreement with expectation, there are five distinct cone angles possible, corresponding to the number of disclinations, m, supported by a graphene sheet. In addition, fine graphic disks are observed as well as wide hollow tubes. Transmission electron microscopy revealed these last common cones were those that correspond to m = 3 and m = 4 disclinations, i.e. cones that are capped by 3 or 4 pentagons. In this paper, we argue that this distribution can be explained in terms of the entropy, that is it is a consequence of the distribution with that has been seeded by monocylic carbon rings, Cx. For large rings with n > 10, we show that most growth modes will result in m = 3, 4 cones.

4:15 P.M. W2.7

MONO-SIZED AND SINGLE-WALLED 4-ANGSTROM CARBON NANOTUBE ARRAYS. N. Wong, G.D. Li, Z.K. Teng, Department of Physics, the Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, CHINA.

Mono-si-sized and single-walled carbon nanotube (SWNT) arrays, synthesized by pyrolysing tripolyphosphine molecules in the channels of porosilite single crystals were synthesized using high-resolution transmission electron microscopy (HRTEM). The SWNT is used as a type of microporous crystal. The one-dimensional channels in the crystals are imaged in vacuum, array have an inner diameter of 0.21 nm. During the initial growth of TRIPOLI, pyrophosphane was introduced into the channels. The subsequent thermal treatment of AFM at 500°C in vacuum led to the pyrolysis of carbon and the formation of SWNTs in the AFM channels. The resulting AFM crystals show good polarization characteristics. While normal AFM crystals are transparent and isotropic in character, SWNTs were extracted by dissolving the AFM framework in HCl acid. The SWNT-containing solution was subsequently enriched and dispersed on carbon ITO film for TEM investigation. SWNTs with a diameter of 0.4 nm, the smallest known to date, have been directly observed and confirmed by imaging simulations. HRTEM images of these ultrasmall-SWNTs were imaged as paired fringes. The spacing and shape of the paired fringes are sensitive to the focus condition of HRTEM. Imaging when being done at Scherzer defocus condition, the spacings between the paired dark fringes (outside-to-outside) represent the actual diameters of the SWNTs.

4:30 P.M. W2.8

SPONTANEOUS FORMATION AND STABILITY OF GaP CAGE STRUCTURES: A THEORETICAL PREDICTION OF A NEW FULLERENIC F-BUD, Department of Theoretical Chemistry, Vrije Universiteit, Amsterdam, THE NETHERLANDS; V. Tozzi, INFN and Scuola Normale Superiore, Pisa, ITALY; A. Fracisco, Institute of Theoretical Physics, University of Nijmegen, Nijmegen, THE NETHERLANDS.

The discovery of carbon fullerenes and nanotubes has opened a completely new field at the borderline between chemistry and physics leading to many new phenomena and applications. One intriguing question is whether fullerene cages could be realized in typical semiconductors of the III-V family, like GaAs, InSb or GaP, which do not show a graphene-like bulk structure. We report the spontaneous formation of a GaP fullerene cage in ab initio Molecular Dynamics simulations starting from a bulk fragment. A systematic study of the geometric and electronic properties of neutral and ionized GaP clusters up to 28 atoms shows how the stability of hetero-structures is strongly affected by the presence of boron nitride and carbon fullerenes of the same size; the clusters are thermally stable up to a temperature range of 1500-2000 K and do not dissociate and remain in the same structure when ionized. This work might stimulate experimental observation of hetero-fullerenes also to III-V semiconductor compounds.

4:45 P.M. W2.9

SWNT NUCLEATION-ENERGETICS OF ZIPPING-EDGE MECHANISM. Shwu Y. Reckin, Beckman Institute, UIC, Urbana, IL; Ioffe Institute, St. Petersburg, RUSSIA.

It is intriguing that, despite of the years of experimental study and theoretical modeling, formation of SWNTs is not explained. SWNT nucleation is one of important questions to the theory because the growth might not change nucleation helicity or radius. In the fact that the fact that cluster configuration is "frozen" at typical synthesis conditions: temperature, growth rate, density, entangled structure of raw material etc. The nucleation with hemispherical bowl is shown to be the rare event being on the growth thermodynamics. The main reason is that creation of pentagons in the graphene lattice costs large energy. This prohibits the curved construction at low number of carbon atoms N ≥ 250. Moreover, the curved lattice is unstable to scatter into complete sphere which is the end of the SWNT nucleus evolution. Anisotropy of the SWNT growth is also puzzling in
view of proposed formation from isotropic/amorphous graphene/graphite. Our novel model naturally explains the nucleation of 1D domains. The generality of our model is given by the edge of graphite layers. The most stable is the zigzag ([100]) edge of graphite. Hence, the most probable is the formation of [011] (nanotube) nucleus making right angle to this edge. Our theory predicts for the first time the stability of SWNTs of preferred helicity from purely macroscopic consideration. Thermodynamics of the edge zigzag shows that the optimal diameter of cylindrical nucleus is about 1.5 Å depending on the ratio of elastic strain to van-der-Waals interaction energy. The strength dependence of the yield stress that gives initial graphene material owing to the zigzag happens when the nucleus cylinder meets sp² lattice defect intersecting two adjacent layers of graphite. Summarizing, our novel mechanism explains the proposed formation of nanotube nuclei with diameter 1.5 Å which is fairly close to experimentally found [10,10] SWNTs.

SESSION W3. NANO TUBE SYNTHESIS II

Chair: David B. Geoghegan and Andrew G. Rinzler

Wednesday Morning, April 18, 2001

Metropolitan 1 (Argent)

8:30 AM W3.1
SYNTHESIS OF VERTICALLY ALIGNED CARBON NANOFIBER FILMS BY RF MAGNETRON SPUTTERING. Koo-Yi Lee, Kenichi Fujimoto, Shigeki Inoue, Shun-ichi Honma, Kenjiro Osumi, Osaka Univ, Dept of Electronic Engineering, Osaka, JAPAN.

Here we show a novel method to synthesize the aligned carbon nanofibers. Recently, carbon nanofibers and nanotubes have drawn a great attention because of their unique electrical, chemical, and mechanical properties. Especially, the electron field emission property considered in detail the alignment of the carbon nanofibers. From the application, aligned carbon nanofibers have been used as an emitter for flat panel displays. In this study, the aligned carbon nanofibers were grown by using a RF magnetron sputtering system with a tungsten filament. The target was a 99.999% pure carbon disc and nitrogen gas was introduced to the chamber to create a plasma by applying RF power at a relatively low pressure of 2 × 10⁻³ Torr. Silicon wafers were used as substrates. Before attaching the substrates to the chamber, the Si substrates were etched by electron beam evaporation system and then the Ni/Si substrates were treated by HF dilution to make the Si surface uneven. The sputtering deposition was carried out at a substrate temperature of 700°C. The tungsten filament temperature was up to 2000°C during the deposition. Surface morphology, carbon structural features, and chemical composition were investigated by SEM, XRD, and XPS respectively. According to SEM observations, they showed dense nanofibers were grown vertically on the substrates, and nano particle was formed on the top of each fiber. The diameters and the density of the fibers were in the range from 30 to 50 nm and about 10⁶ to 10⁷ cm⁻², respectively. More details of the effect of tungsten filament on surface morphology, structure, and chemical properties of the carbon nanofibers will be discussed in this paper.

8:45 AM W3.2
PREPARATION OF CARBON NANOTUBES BY USING MESOPOROUS SILICA. Shinji Kawasaki, Shingo Komiyama, Shigekazu Okmori, Akifumi Yoo, Fujio Okino, Hirokazu Toshara, Department of Chemistry, Faculty of Textile Science & Technology, Chisushi University, Niigata, JAPAN.

Carbon nanotubes have attracted much attention, not only because of their elegant structure, but also because promising applications of the nanotubes have been demonstrated including electronic field emission sources and nano-electronic components. Although there are many methods to prepare the nanotubes such as laser-ablation and arc-discharge, the most important problems is how to prepare nanotubes with desired form. Another significant problem is how to obtain such nanotubes in a large scale. Here we report the new preparation method using mesoporous silica whose mesopore size is controllable in the wide range of 2 nm to 30 nm as the possible solution of the above problems. Mesoporous silica with mesopores of 2.5 nm and 7.3 nm in diameter were synthesized in the presence of cetyltrimethylammonium bromide (CTAB, Akrich) surfactant and triblock (poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPPO-PEO) copolymer (Pluronic P123, BASF), respectively. Trimethylbenzene (TMB) was used as an organic swelling agent to enlarge the mesopore. Calcination was carried out by slowly raising temperature from room temperature to 600°C X-ray powder diffraction patterns, N₂ adsorption-desorption isotherms at 77 K, transmission electron micrograph images were measured to characterize the materials obtained. Carbon deposition on the mesoporous silica was performed by the decomposition of propylene gas at 800°C. N₂ was used as a carrier gas. The mesoporous silica with carbon deposition was washed with an excess amount of HF solution to dissolve organics. We confirmed by TEM observation that carbon nanotubes with homogeneous diameter can be obtained by the present method.

9:00 AM W3.3
SINGLE WALL CARBON NANOTUBES: SOME RECENT RESULTS ON THE PRODUCTION AND PROCESSING. Patrick Bernard, Ingrid Stepanek, Robert Almaric, Vincent Jourdain, G. Tey. Univ. of Montpellier, U. G. Villig, Alain Pénard, Philippe Poulin, CRPP, CNRS, Pesca, FRANCE; Marion Becher, Michael Hirsch, Siegmund Roth, Max Planck Institute, Stuttgart, GERMANY.

Single wall carbon nanotubes (SWNTs) for technological applications demand various improvements before utilization: (i) better production yield and scale quality, (ii) various processing techniques to transform the initial mix of multi and long nanotubes into a usable material. While the HPCCO (CO disproportionation) process appears to be the best solution in the near future for large scale production of SWNTs, the sublimation of carbon using the electric arc is still interesting for small scale production (a few grams per day), due to its low price and easy handling. We will review the most recent developments of this method, particularly in what concern the catalytic systems used and their effect on the nanotube characteristics. Processing is necessary to adapt the raw material to a given application. Two processes will be presented. First, cutting the nanotubes will allow the inside volume to be accessible for storing atoms and molecules. The situation concerning hydrogen storage in such systems will be analyzed and discussed. Second, the making of macroscopic fibers and ribbons from SWNTs is one essential step for producing high strength amorphous materials. We will describe the process to obtain such systems and their characteristics.

9:30 AM W3.4
CHEMICAL ROUTES TO NANO TUBE PHYSICS AND DEVICES. Hongjie Dai, Department of Chemistry, Stanford University, Stanford, CA.

In the first part of the talk, I will present recent work in controlled growth of multi-walled (MWNT) and single-walled nanotubes (SWNT) with ordered structures on surfaces. These growth approaches involves chemical vapor deposition on catalystically patterned substrates. In the second part, I will show that controlled growth allows for integration of nanotubes into functional devices. The electronic, mechanical and electromechanical properties of nanotubes can be systematically addressed. Some of our latest results in ballistic transport in nanotubes, high temperature single-electron transistors and inelastic junctions showing rectifying and Enkak diele behavior will be presented.

10:00 AM W3.5
BuckyTUBES NEW COMMERCIAL MATERIALS. Daniel T. Colbert, Carbon Nanotechnologies, Inc., Houston, TX.

The tubular extensions of the fullerenes popularly known as “Buckytubes” are now available commercially. Early measurements indicate that these tubes behave as coherent quantum wires. In short lengths they are expected to be the most rigid of all possible beams and effectively unbreakable even when bent in half. Growing in long lengths they are expected to form the strongest fiber ever known with a tensile strength approximately 100 times stronger than steel at only one-sixth the weight. Short lengths derivatized at the ends will constitute a new branch of organic chemistry. These Buckytubes may bring into reality old dreams of molecular electronics, and some application in virtually all technologies where electronics flow. Assembled in closely-packed crystalline arrays these tubes will serve as “need crystal” for the direct, continuous growth of super-conducting, light-weight membranes, plated structures and dissimilar silica entirely out of carbon. This talk will highlight both the sustained promise of Buckytubes, and the steps that Carbon Nanotechnologies, Inc. has taken toward their commercialization.

11:00 AM W3.6
CARBON NANO TUBE AND NANO FIBER BASED DEVICES. Michael Simpson, David Geoghegan, Michael Guillorn, Douglas Lindes, Alex Parsekian, David Reis, Vladimir Markovic, Shane Bromley, Darren Ellis, Larry Baily, Phil Brit.

The device research community has become extremely interested in carbon materials (e.g. diamond, hot filament CVD carbon, multiwall and single carbon nanotubes, and carbon fibers) for a variety of electronic, sensing, and actuating device applications. In particular, multi-wall and single wall carbon nanotubes (MWNTs and SWNTs) have electrical and structural properties that may play key roles in the practical development of nanoelectronic and nanosensing devices.
However, the mere existence of these properties is not enough to ensure that practical nanocarbon devices will follow directly from the significant nanocarbon science and mesoscopic physics research. In particular, the need is the accessibility of the desirable properties of MWNTs and SWNTs. For example, both semiconducting and metallic SWNTs can be fabricated and are of considerable potential value in device applications. However, separating the semiconducting tubes from the metallic SWNTs in a manner consistent with the mass production of devices is a considerable challenge. Furthermore, the precise placement and interconnection of carbon nanotubes (or any nanoscale components) ruling mesoscopic-scale devices is difficult. However, vertically aligned carbon nanofibers (VACNFs) overcome some of these challenges. VACNFs are catalytically grown from metal nanoparticles in a PECVD process. The placement and diameter of the catalytic particle, and the duration of the growth time control the position, the diameter, and the length of these fibers. Therefore, VACNFs are beginning to find application in field-emission devices (e.g. flat panel displays and vacuum microelectronics), sensors, and actuators. This lecture gives an overview of the practical realization of nanoscale devices with SWNTs, MWNTs, and VACNFs. This will include a review of the considerable on-going device research in this area, including our work with SWNTs and VACNFs.

11:30 AM W3.7

DETERMINISTIC GROWTH OF VERTICALLY ALIGNED CARBON NANOFIBERS [VACNFs] FOR NANOSCALE VACUUM ELECTRONIC DEVICES, Douglas H. Lowndes, Vladimir I. Merkulov, M.A. Guillorn, M.L. Simpson, Oak Ridge Natl Laboratory, Oak Ridge, TN.

We recently reported a method for completely deterministic growth of individual vertically aligned carbon nanofibers (VACNFs), by utilizing plasma enhanced chemical vapor deposition (PECVD) in combination with evaporation and precise lithographic placement of nanoscale metal catalyst dots [1]. Vacuum electronic devices utilizing VACNF field emitters are potentially useful in many sensing, actuation, and signal processing applications, but to realize their promise it is essential that mutually compatible methods be developed [2] to fabricate the nanoscale electronic structures needed to control emission, and (ii) to accurately center and grow VACNF emitters within them. In this paper we describe a hybrid process in which a combination of high-resolution electron beam lithography (EBL) and subsequent photolithography has been used, together with conventional micro/nano-fabrication techniques (oxide deposition, metallization and lift-off, RIE), to produce gated electron structures, followed by PECVD growth of single VACNFs centered within these structures [2]. Issues associated with the fabrication and performance of such field emission devices will be discussed and further research needs outlined.


This work was carried out in part at the Cornell Nanofabrication Facility (supported by the NSF under grant no. DMR-9621291), and at Oak Ridge National Laboratory (ORNL), with support from DARPA/MTO under contract no. 1808/S2X and from the ORNL LDRD program. ORNL is managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract no. DE-AC05-84OR21400.

11:45 AM W3.8

CONTROLLING STEPS DURING EARLY STAGES TOWARD ALIGNED CARBON NANOTUBES BY MICROWAVE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION, C.Y. Wen, L.C. Chen, National Taiwan University, Center for Condensed Matter Sciences, Taipei, TAIWAN; C.S. Shen, Y.F. Chen, National Taiwan University, Department of Physics, Taipei, TAIWAN; K.H. Chen, Academia Sinica, Institute of Atomic and Molecular Sciences, Taipei, TAIWAN.

While it is now relatively easy to generate aligned carbon nanotubes (CNT), a form of tremendous interest in microelectronic applications, the key steps that control the aligned growth of the CNT is yet an open question. In the present study, well-aligned CNTs have been grown by microwave plasma enhanced chemical vapor deposition (MPECVD) on silicon substrates pre-coated with thin layers of transition metals, such as Fe, Co and Ni. Both high-resolution transmission electron microscopy and field emission scanning electron microscopy have been employed to study the structural evolution of the CNTs during the early stages of CNT growth. Effects of processing gas composition as well as the pre-coating catalytic layer characteristics, such as the type of catalyst, crystallinity and layer thickness, have been investigated. It is observed that the growth rate of CNTs can be significantly enhanced by adding nitrogen in the MPECVD process. Most interestingly, the very first key step toward growth of aligned CNTs is the formation of high-density fine carbon onion encapsulated metal (COEM) particles. Furthermore, the formation and the size of the COEM particles were strongly affected by the crystallinity and the thickness of the catalytic layer, regardless of the type of the catalyst used. Some mechanisms of the aligned CNT growth could be proposed from these mesoscopic observations.
2:30 P.M. W4.4
WEAR CHARACTERISTICS OF ETCHED SILICON AND CARBON NANOTUBE AFM PROBES. T. Larsen, K. Moleni, M.G. Lagally, Piezomax Technologies, Madison, WI.

The drive to create smaller and faster microelectronics has created a need to image features with increasingly larger aspect ratio. The ability of etched silicon tip tapping mode AFM probes to resolve high-aspect ratio features is limited by the tip half angle on the leading side. By this reason, carbon nanotube probes, which essentially have a tip half angle of zero, are much more effective at imaging high-aspect ratio features. We demonstrate the versatility of carbon nanotube AFM probes in imaging high-aspect ratio features and very narrow lines in photo- and x-ray lithography patterned structures without sample damage. Rate of wear also limits the cost-effective use of etched silicon probes. Experiments to characterize the rate of wear of both etched silicon and carbon nanotube probes have been performed on CVD-cube sample surface. The rate of wear is measured as the change in tip diameter relative to scan age as observed by TEM. We have found that carbon nanotube probes have a much lower rate of wear then etched silicon probes, with a useful life of the nanotube probe at least an order of magnitude greater. The wear characteristics of both types of probes will be quantitatively compared. Finally, the much lower sample damage caused by the nanotube probe will be described.

Supported by DARPA, SHRI Programs.

2:45 P.M. W4.5
PHYSICAL INTERACTIONS OF CARBON NANOTUBES AND CONJUGATED POLYMERS. Alan B. Dalton, Hugh J. Byrne, Dublin Institute of Technology, Facility for Characterization and Spectroscopy (FOCAS), Dublin, IRELAND; Jonathan N. Coleman, Brenda D. Doherty, Werner J. Bhu, University of Dublin, Materkirk Ireland Research Centre, Dept of Physics, Dublin, IRELAND; Polickel M. Agyan, Rensselaer Polytechnic Institute, Dept MSE, NY.

Hybrid systems of both multi-walled and single-walled carbon nanotubes and a range of conjugated polymers have been studied using electron spin resonance, absorption and emission spectroscopy, electronic microscopy and Raman scattering. The relative strength of the interaction was seen to depend mainly on backbone conformation and the persistence (absence) of covalently attached side-groups. In particular, the solubility of poly(phenylenevinylene-co-2,5-dicyanotetraylene) was shown to be capable of suspending nanotubes indefinitely whilst the accompanying amorphous graphite settles out. In the case of single-walled nanotubes, electron microscopy and Raman scattering indicate that through an intercalation process, ropes of nanotubes are destroyed resulting in individual nanotubes being well dispersed within the polymer matrix. Moreover, Raman and absorption studies suggest that the polymer interacts preferentially with nanotubes of specific diameters or a range of diameters. Hybrid systems of a cyano- and iodinated PPV and carbon nanotubes were also studied. Absorption, emission and Raman spectroscopy indicate a strong electronic interaction of the polymer: The polymer is seen to tune resonant Raman cross-sections for specific tubular modes in the polymer layer and low density absorption of some tubes are reduced (or enhanced). These changes are accompanied by quenching of the polymer luminescence similar to phenomena witnessed in composites of conjugated polymers and C60.

3:30 P.M. W4.6

Two developments from our recent work having potential technological significance will be presented. First, these involve the finding that Raman spectral lines from oriented single-wall carbon nanotubes (SWNT) are strongly polarized along the nanotube axis. This is due to a strong anisotropy in the polarizability dependence of the resonant absorption (which is responsible for the large resonant Raman signal from SWNT). This permits a straightforward analysis of single nanotube polarized Raman data for quantifying the degree of alignment in oriented samples. 1 It will also describe the state of our understanding and progress in the development of SWNT actuators, based on an essentially new electro-mechanical transduction mechanism first identified in 1990.2


4:00 P.M. W4.7
CHEMICAL ADSORPTION OF POLYMER ON CARBON NANOTUBE. Chengyu Wei, Kyungsung Cho, Department of Mechanical Engineering, Stanford University, CA; Depak Swartzendruber, NASA Ames Research Center, Moffett Field, CA.

Recently carbon nanotubes are considered as nanoscale fibers which can strengthen polymer matrix. Nanotubes reinforced polymer matrix composite materials can be used for micron scale devices with enhanced chemical functionality and smart polymer coating to protect materials under extreme physical conditions such as microenvironments. 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 work we study the chemical bonding between polymer molecules and carbon nanotubes (CNT) using molecular dynamics. Study shows that the bonding between polyethylene 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. We will discuss about the resulting mechanical coupling between the CNTs and polymer matrix to develop an efficient nano-composite materials.

4:15 P.M. W4.8
AB INITIO CALCULATIONS OF THE SWNT/METAL INTERFACE. Shu Peng and Kyungsung Cho, Dept of Mechanical Engineering, Stanford University, Stanford, CA.

Carbon nanotubes have shown great potential in electronic and structural applications due to their unique mechanical, electrical and chemical properties. Carbon nanotubes are ideal templates for the growth and assembly of a variety of nanoscale materials. In this paper, adsorption properties of different metal (Al, Ti) on (8,0) Semiconducting Single Walled Carbon Nanotube (S-SWNT) have been investigated through first-principle pseudopotential calculations. Five different adsorption configurations for Ti and Al have been simulated separately, and the adsorption energy was calculated using density functional theory, and it is found that the Al/SWNT(8,0) and Ti/SWNT(8,0) interfaces have quite different features. The nature of the metal deposition on SWNT and surface coverage have been simultaneously considered, and the effect of tip curvature was also considered. The study is focused on SWNTs with Ti and Al adsorption. The results show that Ti and Al are the metals that can strongly bond with SWNTs, while other metals like Cr, Fe, Ni show no significant interaction with SWNTs.

4:30 P.M. W4.9
ATOMIC SIMULATION OF CARBON NANOTUBE ROPES: STRUCTURE, STRENGTH, AND THERMAL TRANSPORT. Ju Li, Sidney Yip, Massachusetts Institute of Technology, Department of Nuclear Engineering, Cambridge, MA; Joshua Fujikawa, Honda R&D Co., Ltd., Wako Research Center, JAPAN.

Using Brenner type Reactive Empirical Bond Order (REBO) interatomic potentials, we perform atomic simulations to calculate the optimized structures, tensile and bending strengths, and thermal conductivities of both straight and twisted single-walled nanotube ropes (bundles). Specific properties under investigation are: 1. the stacking of straight SWNTs. 2. How strong are twisted ropes compared to the sum of its components. 3. Realistic thermal conductivities of SWNTs and their bundles, where we check direct simulation against the Green-Kubo linear response theory.

4:45 P.M. W4.10
GROWTH OF CARBON NANOTUBES FROM LIQUID PRECURSORS. Wei Li and Karim Salama, Texas Center for Superconductivity and Department of Mechanical Engineering, University of Houston, Houston, TX.

The most commonly used techniques for synthesizing carbon nanotubes exploit either the vapor of single carbon-containing molecules (e.g. C6H6 and CH3OH) or carbon plasma created by fine wires ablation and arc discharge. Although these techniques have proved to be effective, many structural features in large carbon-containing molecules (e.g. benzene rings) which assume similarities with the structures of fullerenes cannot be used since these molecules are normally in the form of liquid. The present work deals with the development of a technique which demonstrates the feasibility of growing carbon nanotubes directly from such carbon containing liquid precursors. This technique involves the conversion of the liquid, which are then transferred to heated quartz substrates coated with Ni nanoparticles. The Ni nanoparticles are synthesized by direct decomposition of Ni acetate on quartz in reducing atmospheres at temperatures between 200-500 °C. The result show that multi-walled carbon nanotubes with diameters between 20-50 nm.
nm can be grown at 650 - 800°C. These results also suggest the possibility of making use of certain structural features in large organic molecules as building blocks of carbon tubes. In the second, the system developed is non-vacuum based and capable of delivering high volume of fine aerosol per unit time, this method can also have implications on large-scale production of carbon nanotube related devices.

SESSION W5: NANOTUBE ELECTRONIC AND STORAGE APPLICATIONS
Chairs: Michael L. Simpson and Rodney S. Ruoff
Thursday Morning, April 19, 2011
Metropolitan I (Argent)

8:30 AM *W5.1

In this talk we present recent results on the effects of processing on the Li storage capacity of SWNTs. Electrochemistry and solid state nuclear magnetic resonance measurements showed that the reversible Li storage capacity of purified SWNTs increased from LiC6 to LiC9 after chemically etching. All the SWNTs become metallic upon Li intercalation with the electronic density of states at the Fermi level increasing with increasing Li concentration. We will also present results from electrochemical, x-ray and Raman studies of Li reaction with nanostructured Si (poly-Si). The electronic density barriers for formation of Li-Si alloys are significantly reduced. Reversible electrochemical reaction takes place at room temperature, about 400K below what is possible for bulk Si. The high Li concentration and low electrochemical potential with respect to Li/Li+ make n-Si attractive for Li storage applications.

9:00 AM *W5.2

Single wall carbon nanotubes have elastic properties that are unprecedented for a molecular solid. Through measurements of the specific heat, we have recently verified the prediction that confinement of sound waves (phonons) to the molecular cylinder leads to an energy spectrum consisting of quantized one-dimensional subbands, and discovered that this quantization is only weakly perturbed by tube-tube mechanical coupling in "real-world" nanotube bundles. [1] These findings support the prediction that nanomaterials have an extremely large thermal conductivity. Along with the specific heat measurements, we will present thermal conductivity measurements of aligned, density-matched nanotube bundles and explore possible applications of this nanomaterial to thermal management. [1] J. Hone, B. Bulloch, Z. Benes, A.T. Johnson, and J.E. Fischer, Specific Heat of single-wall carbon nanotubes: phonon quantization in a nanoscale material, Science 289, 1,780 - 1,783 (2000).

9:30 AM W5.3
THREE-TERMINAL NANODEVICE WITH MULTIPLE FUNCTIONALITY. E. Leonard, Sandia National Laboratories, Livermore, CA; J. Tersoff, IBM Research Division, T.J. Watson Research Center, Yorktown Heights, NY.

We present a nanoscale three-terminal device based on a single-wall semiconducting carbon nanotube. Calculations of quantum transport show that such a device provides unique device functionality at room temperature. It can operate as a ballistic field-effect transistor with excellent characteristics, and at large gate voltages the device becomes a gated resonant-tunneling triode with tunable negative differential resistance. Hence, a single device can be used for multiple applications.

10:15 AM *W5.4

Carbon single-wall nanotubes (SWNTs) are capable of adsorbing hydrogen at room temperatures and pressures [1]. 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 chemically purifying SWNTs in pure hydrogen at high temperatures which have also been used to activate these materials for hydrogen storage [2]. 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 introduced into the SWNTs during the process. Hydrogen can be stored on activated samples in a matter of minutes at room temperature and pressure to over 5 wt% on a total sample weight basis. Temperature programmed desorption spectroscopy shows two distinct hydrogen adsorption sites [2]. In this work, we present results from high resolution multinuclear Raman spectroscopy to probe how the electronic properties of the SWNTs change with hydrogen exposure, as well as complementary thermopower measurements. This data will be discussed with respect to the mechanism of hydrogen adsorption on the SWNTs. The role of the impurity metal alloy will also be discussed.


11:00 AM W5.5
AB INITIO STUDY OF HYDROGEN ADSORPTION IN CARBON NANOTUBES. Henry Scudder, Gang Li, and Nicholas Kociassell, Department of Physics, California State University Northridge, Northridge, CA.

Hydrogen adsorption in nanotubes has witnessed dramatic growth recently due to its potential for hydrogen storage in carbon nanotubes. First principles electronic structure calculations based on density functional theory can offer the unique insight for the atomic structures and provide reliable energetics for understanding the hydrogen adsorption process. In this work, we have investigated the H adsorption process in a 60 armchair nanotube by placing one and two H atoms at various sites both inside and outside the nanotube. We have also studied the extreme case of saturating all 24 C atoms with 24 H atoms outside the nanotube. For an isolated H atom, we find a strong bonding between the H and the nearest C atom with a bond length about 1.11 Å on both sides of the nanotube, and a description energy of 1.7 eV (outside) and 0.5 eV (inside) per H atom. For the case of the H2 molecule adsorption, the calculations indicate that the orientation of the molecule relative to the nanotube is critical in determining whether the molecule can be adsorbed. For example, if the H2 molecule is perpendicular to the nanotube axis, they form a stable C-H bond with the description energy of 2.5 eV (outside) and 0.7 eV (inside) per H atom. However, if the H2 molecule is parallel to the nanotube axis halfway between two C atoms on the same layer, it is not adsorbed. Interestingly, the H adsorption on the outside of the nanotube is energetically much more stable than the adsorption on the inside. The configuration of 24 H atoms attached to the exterior of the nanotube is found to be stable with an adsorption energy of 0.84 eV per H atom.

11:00 AM W5.6
SEPARATION OF HYDROGEN ISOTOPES IN CARBON NANOTUBES. David S. Shull, Anastasios Skoulidis, Dept. of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA; Srinivasa Chandra, Vladimir Simonians and J. Noel Johnson, Dept. of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA.

Standard applications of molecular sieves can separate chemical species based on differences in molecular size. From a classical point of view, molecular sieving cannot separate isotopic species. We have recently shown that a mechanism known as quantum sieving can be used to separate isotopic species by adsorption in microporous materials [1]. Quantum sieving takes advantage of the fact that the de Broglie wavelength of a molecule is dependent on the isotopic identity of the molecule. We have performed an extensive computational study of quantum sieving of hydrogen isotopes adsorbed in carbon nanotubes and nanotube bundles. Our results predict that nanotubes can be extremely effective for separating hydrogen isotopes. We will discuss the role of nanotube diameter on adsorption strength and isotope selectivity. We will also discuss the accuracy of the density functional theory of multi-component adsorption such as Ideal Adsorbed Solution Theory by comparing these theories with explicit multi-component adsorption simulations. Our results will be compared with experimental observations in zeolites from the literature. Time permitting, we will also discuss
11:15 AM W5.7
INTERCALATION OF LITHIUM INTO SHORTENED SWNTS BY ELECTROCHEMICAL METHOD. B. Gao, Curriculum in Applied and Materials Science, University of North Carolina at Chapel Hill, Chapel Hill, NC; H. Shimoda, L. Fleming, Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, NC; O. Zhou, Curriculum in Applied and Materials Science, Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, NC.

Purified SWNTs were cut to short bundles and acid oxidation were intercalated with lithium by electrochemical method. The cut SWNTs show enhanced electrochemical properties compared to purified SWNTs. The irreversible lithium storage capacity of the shortened SWNTs (Li/C) is about twice that of purified SWNTs (∼Li/C), while the voltage hysteresis between intercalation and de-intercalation is 4V smaller. Structure study shows that the average bundle length can be controlled by the oxidation time. Oxidation also introduced disorder within SWNT bundles. The results show that cut SWNTs are promising for lithium or hydrogen storage.

11:30 AM W5.8
FIRST-PRINCIPLES STUDY ON LITHIUM ABSORPTION IN CARBON NANOTUBES. Yi Lin, H. Yamasaki and M. Morigi, Nagoya University, Dept. of MESE, Nagoya, JAPAN.

Carbon nanotubes are attractive materials because of a variety of potential applications not only to structural and electronic materials, but also to energy storage materials, for example, the electrodes for a rechargeable Li-ion battery and a lithium capacitor. Recently it has been reported that lithium could be intercalated electrochemically in the carbon nanotubes. In particular, single-walled carbon nanotubes show both high reversibility and irreversible capacities as the electrodes for the rechargeable Li-ion battery. However, the mechanism for the high lithium absorption in carbon nanotubes has not been clarified yet. In this study, several lithium occupancy sites on the single-walled carbon nanotubes are assumed, and the lithium absorption energy and the electronic states are investigated using molecular orbital methods. The mechanism for the lithium absorption in the carbon nanotubes is also discussed with the aid of the electron theory.

11:45 AM W5.9
AN NMR STUDY OF SWNT, TUBE-TUBE INTERACTION, GAS EXPOSURE AND ALKALI-METAL INTERCALATION. X. P. Tong, H. Shimoda, A. Kleinhans, L. Fleming, B. Gao, O. Zhou, Y. Wu, Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC.

The 13C nuclear magnetic resonance (NMR) technique has been successfully used to measure quantitative value of the electronic density of states at the Fermi level (g(EF)) of the metallic tubes in single-walled carbon nanotubes (SWNTs). The (13C,13C) spin-spin relaxation rate (1/T2) of the semiconducting tubes is determined and the dielectric behavior of the metallic basis in SWNT bundles and fuses the tube-tube interactions. At one atmosphere pressure and room temperature, we observed that the 13C 1/T2 is significantly affected by the exposure of the SWNT bundles helium gas but not other inert gas. Our study also found that the intercalation of alkali metals into SWNT bundles substantially changes the g(EF) of the SWNTs.

SESSION W5: FIELD EMISSION
Chairs: Douglas H. Lowndes and John Robertson
Thursday Afternoon, April 19, 2001
Metropolitan I (Argent)

130 P.M. #W6.1
FROM NANOCRYSTALLINE DIAMOND TO NANOTUBE FIELD ELECTRON EMITTERS. Oliver Groening, Lars-Ola Nilsson, Pierangelo Groening, Louis Schlagel, University of Freiburg, Physics, Sica Dept., Freiburg, SWITZERLAND; K耐neth A. Dearn, Motorola Inc. Res., Tempe, AZ.

Carbon has attracted in the recent years a great deal of interest in the area of field electron emission. The search for low cost solutions to fabricate planar electron emitters for use e.g. in field emission flat panel displays (FED) can be regarded as the main driving force behind the research effort on carbon field emitters. In the first part of the talk we like to review and discuss the field emission properties of nanocrystalline diamond, diamondlike carbon and carbon nanotube. We show that field emission plays a key structural role in the field emission of all these carbon films. In the second part the emission properties of carbon nanotubes will be discussed in greater detail. Special attention is brought to scanning mode field emission measurements and the concept of field enhancement distribution functions (FEDF) in order to obtain a meaningful characterization of planar field emitters. We will show how we experimentally measured FEDFs can be used as inputs for simulation of emission site densities. We discuss the requirements of field emitter thin films towards optimum field emission performance. The field emission of single walled carbon nanotubes is discussed on a more fundamental basis. We address the issue of work function changes due to site effects at the cathode apex and we will discuss the possibilities that thermo-field emission offers in order to investigate the work function, the shape of the field emission barrier and the nature of the field emitting states.

2:00 PM W6.2
FIELD EMISSION PROPERTIES OF CARBON NANOTUBE CATHODES. Chris Bower, Wei Zhu, Sungjoon Jin, Lucent Technologies, Bell Laboratories, Murray Hill, NJ; Otto Zhou, Univ. of North Carolina, Dept. of Physics, Chapel Hill, NC.

We have studied the field emission from a variety of carbon nanotube cathodes. These include films of randomly aligned single-walled carbon nanotubes made by pulsed laser ablation, and films of highly oriented multi-walled nanotubes made by microwave plasma-enhanced chemical vapor deposition. We will compare the current-voltage behavior, lifetime and emission site densities of various nanotubes cathodes. All of the nanotube cathodes were found to emit technologically useful current densities of 10 mA/cm2 in macroscopic electric fields between 1-5 V/micrometer. In addition, nanotube cathodes are capable of generating stable current densities in excess of 4 A/cm2.

2:15 PM W6.3
SCANNING-PROBE FIELD-EMISSION STUDIES OF RANDOM FORESTS AND ORDERED ARRAYS OF VERTICALLY ALIGNED CARBON NANOFIBERS. Vladimir I. Morko, Douglas H. Lowndes, Larry R. Beiler, Michael L. Simpson, Oak Ridge National Laboratory, Oak Ridge, TN; Michael A. Guillem, E. Darren Ellis, Univ. of Tennessee, Dept. of Electrical Engineering, Knoxville, TN.

Random “forests” and patterned arrays of vertically aligned carbon nanofibers (VACNFs) were grown utilizing dc plasma-enhanced chemical vapor deposition (PECVD). Field emission (FE) measurements were performed using a scanned current probe with variable diameter as low as ~1 um. The probe was scanned in directions perpendicular and parallel to the sample plane, which allowed measuring not only the emission turn-on voltage at fixed locations but also the emission site density over large surface areas. The results show that dense forests of VA-CNFs are not good field emitters as they require high extracting fields. This is attributed to the electric field screening by the neighboring VACNFs. In contrast, sparse forests exhibit moderate-to-low turn-on fields as the screening effect is much less pronounced in this case. Ordered arrays with variable distance between isolated VACNFs were also studied, and emission from the isolated VACNFs was observed. VACNFs are found to exhibit very large maximum FE current and long FE lifetime, all being important for practical applications.

2:30 PM W6.4
FIELD EMISSION FROM SHORT AND STUBBY NANOTUBES. Manish Chhowalla, Nalan Rupesinghe, Ken Teo, Caterina Ducati, John Robertson and Gehan Amaratunga, Engineering Dept., University of Cambridge, Cambridge, UNITED KINGDOM.

Vertically aligned nanotubes are of great interest for field emission, electrochemistry and energy storage. Well aligned nanotubes can be grown using plasma-enhanced chemical vapor deposition. Generally, Ni or Co layers are used as catalytic layers for the growth of nanotubes. By adjusting the growth parameters such as the thickness of the catalyst layer, acetone to ammonia ratio and the deposition temperature, the size, length and the density of the nanotubes can be controlled. Field emission from forests and sparsely populated nanotubes were measured. High turn on fields (~10 V/µm) were found for these forests while the sparsely populated nanotubes showed a lower turn on field. The most interesting result however was that short and stubby but sparsely populated nanotubes showed a lower threshold field and a higher saturation current density then their longer counterparts. We offer a possible explanation for this.

2:45 PM W6.5
FIELD EMISSION SITE DENSITIES OF NANOSTRUCTURED CARBON. J. B. Cui, J. Robertson, W. A. Miller, Cambridge University, Cambridge, UNITED KINGDOM.
The field emission properties of nanostructured carbon films deposited by cathodic vacuum arc at room temperature have been investigated by measuring the emission currents and the emission site density. The films have an onset field of 3 V/\mu m. The emission site density is viewed on a phosphor image and it increases rapidly with applied field. The work function of these films has been measured by Kelvin probe method and is always about 4.2 eV. This is similar to the field enhancement factors having an exponential distribution. Vertically aligned carbon nanotubes (CNTs) were grown by a CVD-PECVD method to fabricate gated field emitter arrays and diode emitters. Gated emitter substrates were made on glass as follows: Cr was deposited and patterned into lines as a cathode, and amorphous Si was deposited onto Cr. 1 μm thick SiO2 was deposited electrostatically between cathode Cr and gate Cr deposited onto SiO2. Holes were made through gate and insulator with a diameter of 4 μm. Finally, catalytic Ni film was deposited into exposed cathode holes. A diode substrate has the same layer structure with that of the gated substrate but no patterns on it. CNTs were deposited onto diode and gated substrates at the same time to compare and analyze the growth properties. The higher growth rates of CNTs are observed in the gated substrate than in the diode substrate at high plasma power. On the other hand the lower growth rates are observed in the gated substrate at relatively low plasma powers. Detailed differences will be presented here.

4:30 PM W6.7
ELECTRON FIELD EMISSION PROPERTIES OF CARBON NANO-TUBES IN. Lin, Materials Science Center, National Tsing-Hua University, Taiwan; T.F. Kuo, C.C. Chi, Department of Physics, National Tsing-Hua University, Hsinchu, Taiwan; K.R. Yue, T.S. Liu, Dept of Physics, Chung-Yuan Christian University, Chung-Li, Taiwan; Z.Y. Jung, Department of Engineering Materials Science, National Tsing-Hua University, Hsinchu, Taiwan, C.H. Tsai, M.D. Chang, Department of MSE, National Tsing-Hua University, Hsinchu, Taiwan; K.S. Luie, H.F. Cheng, Dept of Physics, Nat’l Normal Univ, Taipei, Taiwan.

Carbon nanotubes (CNTs) possess marvelous electron field emission characteristics, including low turn-on field and large emission current density, and have thus been widely investigated for applications as electron emitters in field emission display. While the growth rate for CNTs is fast in arc-discharge process, the yield for CNTs is low. By contrast, laser ablation process can produce high quality single wall carbon nanotubes with high yield, but the conversion rate is low and the characteristics of carbon nanotubes are sensitive to the deposition parameters. A novel process, viz. microwave assisted-CVD process, has been developed to amend the drawbacks of the above mentioned techniques. In this study, a suspension of absorbable microwave and self-generating the heat is used for heating the substrates up to deposition temperature (~1200°C). The reacting gases such as CH4 can thus be easily dissociated, reacting with catalysts coated on the substrates. With such a novel process, the carbon nanotubes can be easily formed on a large substrates (~4 inches). The electron emission properties of the carbon nanotubes vary insignificantly with the processes used for synthesizing the CNTs. The effective work function of synthesized CNTs is around 4.0-12 eV and the electron field emission can be turned on at an applied field of 0.45-1.2 V/\mu m. The CNTs synthesized by microwave assisted-CVD process exhibit the highest electron field emission capability with the highest electron current density, as high as J=12,000 mA/cm² at E=28 V/\mu m applied. It is ascribed to the high CNTs yield and high CNTs density resulted in this process.
N-DOPED C60: DIAMOND FILMS AS A LOW TEMPERATURE THERMIONIC FIELD ELECTRODE SOURCE. F.A.M. KÖCK, J.M. Garguilo, B. Brown, R.J. Nemani, North Carolina State University, Raleigh, NC.

Microwave Plasma assisted Chemical Vapor Deposition (MPCVD) has been utilized to synthesize nitrogen doped diamond films for application as a low temperature thermionic-field emission cathode. The critical result of this study is that the imaging of electron emission from UV photoemission microscopy shows that the samples were imaged in UHV by photoemission microscopy (PEEM) at temperatures up to 900°C and to record the electron emission current in dependence of the applied voltage and substrate temperature. The microscope has 15mm resolution. Nitrogen doped diamond films were grown at substrate temperatures from 850°C to 920°C, microwave power of 13.0W and 50 Torr chamber pressure using 0.5 vol% methane, 12 vol% nitrogen in hydrogen at a total flow rate of 5000cm3. The Raman spectra of the films showed a strong diamond peak at 1332cm−1 and weak signal from the graphitic regions in the sample. Field emission could not be measured at room temperature, but the PEEM images showed relatively uniform emission. The PEEM images showed little change as the temperature increased. At 900°C the T-PEEM and PEEM images are nearly identical in intensity and uniformity. This is to be contrasted with other carbon based cold cathodes in which the emission is observed from only a low density of highly emitting sites. The I/V measurements obtained from the N-doped films in the T-PEEM configuration show a component that depends linearly on voltage at low fields. At higher fields, an approximately exponential dependence is observed. It appears that the emission at low fields could be attributed to thermionic emission of electrons in the conduction band of the diamond. The exponential increase of the current at higher fields indicates a tunneling process. This process may be related to electron emission at the film surface or the supply of electrons at the substrate interface. These results indicate promising new material for the production of low temperature, high brightness electron sources.

SESSION W7 POSTER SESSION
FULLERENES
Chairs: Petra Reineke and Oleg R. Lourie
Thursday Evening, April 19, 2001
8:00 PM
Metropolitan Ballroom (Argent)

W7.1 THE INTERACTION OF C60 WITH GRAPHITE AND BORON NITRIDE: THERMOLUMINESCENCE AND THE INFLUENCE OF DAMAGE ON THE BEHAVIOR OF C60 AILAYERS. P. Reineke, P. Oelhafen, Universit ät Basel, Institut für Physik, Basel, SWITZERLAND; H. Felderhoven, H. Physikalischem Institut, Universität Göttingen, GERMANY.

Understanding the interaction of C60 with different surfaces is an important prerequisite for different applications in the field of C60 thin films. In the present study we investigated the interaction of C60 and damaged C60 films with the surfaces of HOPG (highly oriented pyrolytic graphite) and boron nitride with photoelectron spectroscopy in the ultraviolet (UPS) and X-ray regime (XPS). Subsequent to the deposition at room temperature the films were annealed and the UPS spectra recorded at intervals of 30°C up to a substrate temperature of 800°C. In the first case of an HOPG substrate the desorption is abrupt and completed at 240°C, and the original substrate surface is recovered. The B:N ratio shows a very slow decrease with minimal charge transfer to the substrate and a desorption temperature of 260°C. Only small amounts of C60 remain at the surface, probably trapped at grain boundaries of the nanocrystalline material. For B:N concentrations of 5% or more, the destruction of C60 is achieved even at temperatures as high as 800°C. However, the film does not graphitize completely and the signature of C60 can still be identified after annealing at the highest temperature. To complement this investigation C60 layers were damaged by irradiation with 1 keV Ar ions which leads to a partial destruction of the fullerene layers and allows to relate characteristic spectral changes to the level of accumulated damage. The changes in the electronic properties are comparable to those described for the diamond/amorphous carbon heterogeneous, namely the formation of a Schottky-type barrier.

W7.2 ELECTRICAL TRANSPORT PROPERTIES OF POLYCRYSTALLINE C60 FULLERENE THIN FILMS. Thomas Unold, Matthias Haak, Carola Meyer, Gottfried H. Bauer, Dept of Physics, Univ of Oldenburg, GERMANY.

Polycrystalline C60 fullerene films of approximately 1 micron thickness have been deposited on glass by thermal evaporation in a high vacuum system. The electrical transport was investigated in situ by measuring the photo- and dark conductivity using predeposited coplanar contacts. During illumination with band gap light we observe unusual saturation effects in the photoconductivity, which are followed by the already previously observed long time persistent photocurrent and photoconductivity decay. After the excitation light has been switched off. We present a model which can describe this behavior through the effect of sensitizing centers in the band gap. From the variation of the excitation wavelength and the measurement temperature the energies of the sensitizing centers could be estimated. Finally the effect of the morphology on the electrical transport is studied by varying the grain sizes in the films between 50nm and 0.5 micrometers. The results are discussed in regard to existing models describing transport in poly crystalline thin film materials.

W7.3 NANTAIZED [60]FULLERENECYCLODEXTRIN STAR MOLECULES. Jeong-Seo Park, Han-Chang Kang, Kook E. Gyoedler, Kwangju Institute of Science and Technology, Dept of MSE, Kwangju, SOUTH KOREA.

As [60]fullerene is a very hydrophobic macromolecule, there have been a number of attempts to make it more hydrophilic for biomedical applications. By attaching hydrophilic moieties such as poly(ethylene) chains and cyclodextrin molecules to [60]fullerene, novel water-soluble and biocompatible materials have been successfully prepared. In this study, we report on the synthesis of novel macrocyclic fullerene conjugates which are water-soluble and structured. The telechelic fullerene derivatives have been prepared by addition reaction of poly(ethylene)-obased arms with covalently bonded beta-cycloextrin to [60]fullerene. To this end, a mono-truncated cycloextrin derivative has been prepared in pyridine and then reacted with amino-functional poly(ethylene) in the presence of triethylamine. The subsequent reaction of [60]fullerene with the hydrophilic poly(ethylene)-conjugated cycloextrin derivative yielded the streched micro fullerene after separation and purification procedures. The macrocyclic [60]fullerene derivatives obtained were soluble in water and characterized by UV-VIS, FT-IR, 1H-NMR, and 13C-NMR spectroscopy as well as light scattering measurements, gel permeation chromatography, and thermogravimetric analysis. Due to their hydrophilicity and expected biocompatibility these molecules hold promise for a broad range of biomedical applications.

W7.4 STUDIES ON THE INTERACTION OF WATER-SOLUBLE FULLEROLS WITH BSA AND THE EFFECTS OF METALLIC IONS. Binghe Xu, Xiyung Liu, Xiaoqin Yang, Jihui Qiu, and Weijun Jin*, College of Materials Science and Technology, Tsinghua University of Technology, Beijing, China, CHINA; College of Science, Tsinghua University of Technology, Beijing, Shenzhen, CHINA; Department of Chemistry, Shenzhen University, Shenzhen, China, CHINA.

The interaction of water-soluble C60 derived fullerenol with bovine serum albumin (BSA) in physiological environment was studied in detail by the fluorescence method. Experiments showed that the interaction of fullerenols with BSA is mainly in the manner of non-covalent hydrogen bond. Based on the measurements of fluorescence intensity, the apparent binding constant K and the binding site number n were obtained with K=4000 and n=1, and the energy transfer efficiency in this reaction is 0.68. Besides, the effects of metallic ions such as Cu2+, Fe3+ and Cr(VI) on the interaction of fullerenol with BSA were investigated. It was found that the effects of the metallic ions are quite different from each other. Low concentrations of Cu2+ can promote the interaction between fullerenol and BSA, while high concentrations of Fe3+ and Cr(VI) favor the interactions between fullerenol and BSA.

W7.5 TRANSFORMATION OF ACTIVE CARBON ON ORGANLIKE FULLERENES UNDER ELECTRON BEAM IRRADIATION. Husheng Jin, Binghe Xu, College of Materials Science and Technology, Tsinghua University of Technology, Beijing, Shenzhen, China, CHINA.

The transformation of an active carbon film under Pd nanoparticles to onion-like fullerenes has been in situ investigated by a high-resolution
transmission electron microscope. It was found that the onion-like fullerene/metal polycrystalline film was formed under electron irradiation. The growth process was divided into three steps: first, the flakes of onion-like fullerene were induced by Pt nanoparticles; second, the flakes grew into a few ellipsoidal graphite shell; and third, a gradual reconstruction of the formation of quasi-spherical graphite shells and the bond of Pt particles was took place. It was a composite film of onion-like fullerene and metal particles. It is suggested that the transformation mechanism involves an irradiation of electron and a catalytic effect of Pt nanoparticles, while any temperature rise due to electron irradiation seems to be negligible small.

**W7.6**

**EFFECT OF CRYSTALLINE STRUCTURE AND IMPURITY CONTENT OF CNT THIN FILMS ON THE ORDER/DISORDER PHASE TRANSITION**


Near 260 K, C60 single crystals are known to undergo a first order phase transition, associated with changes in a rotation of C60 molecules. However, the published data dealing with this phase transition in C60 thin films are very contradictory because of the fact that the films grown under different deposition conditions and/or subjected to different post-growth exposures may have substantially various crystalline structure and oxygen content. This paper reports the results of the systematic study of the effect of the crystalline structure and oxygen content of C60 thin films on their structural behavior near the phase transition. C60 films with different structure and oxygen content were obtained by varying the conditions of their vacuum deposition and post-grown annealing. The temperature-resolved X-ray scattering in the temperature range of 300–15 K was used to determine the lattice parameter and its changes near the phase transition. Decrease in grain sizes as well as increase in the oxygen content are found to lead to a gradual reduction of the discontinuity in lattice parameter and the transition temperature.

**SESSION W8: POSTER SESSION**

**NANOTUBE SYNTHESIS**

*Chairs: Rodney S. Ruoff and Alexander A. Puretzky*

Thursday Evening, April 11, 2001

8:00 PM

Metropolitan Ballroom (Argent)

**W8.1**

**CHARACTERISTICS OF CARBON NANOTUBES SYNTHESIZED BY LASER ABLATION PROCESS**

Hsin-Fung Cheng, Chun-Hong Tani, Department of Physics, National Taiwan Normal University, Taipei, TAIWAN; Teng-Fan Kuo, Ming-Hui Chiang, L-Nan Lin, Materials Science Center, National Tsing-Hua University, Hsinchu, TAIWAN; Kun-Ran Yu, Tzen-Hsin Lai, Department of Physics, Chung-Yuan Christian University, Chung-Li, TAIWAN.

Growth behavior of carbon nanotubes (CNTs), which were synthesized with different geometric arrangement between targets and substrates in a laser ablation deposition chamber, was investigated. In conventional laser ablation processes, the substrates were collected in an exhausting port, either using a cooled substrates or electrostatically biased substrates, the yield of CNTs is very high, nearly 100%. However, the deposition rate is very small and the collecting efficiency is extremely low. In modified laser ablation process, the substrates were placed in front of targets to directly collect the species ejected from the targets by laser beams. High deposition rate is achieved, but the yield of CNTs is markedly lower. The CNTs are presumed to form in gas phase in this process, which requires high environment temperature. By contrast, the CNTs are probably grown from the Na clusters coated on substrates in the laser process, which needs substantially lower temperature (annealing temperature). Furthermore, synthesis of CNTs at room temperature is made possible in the modified laser ablation process by exciting the laser induced plasma using high energy laser pulses. The formation mechanism of these processes will be discussed.

**W8.2**

**PURIFICATION OF SINGLE WALL CARBON NANOTUBES PREPARED BY LASER VAPORIZATION FOR ELECTRONIC APPLICATIONS**

Philip F. Britt, David B. Geochagan, Alex A. Puretzky, Henrik Schattenheim, Shane S. Bromley, Xudong Pan, Michael A. Guillom, Derek W. Austin, Michael L. Simpson, and Stephen J. Pennycook, Oak Ridge National Laboratory, Oak Ridge TN; Joseph DeSimone, Department of Chemistry, University of Tennessee at Martin, Martin, TN.

A variety of methods have been developed for the synthesis of single wall carbon nanotubes (SWNT) which have focused on determining the conditions to maximize production rate and purity. Although it would be desirable to produce SWNT of the highest quality, all additional chemical purification treatments are required to remove residual metal catalyst and amorphous graphitic carbon from the SWNT. We are currently interested in the production of SWNT for electronic and optoelectronic applications. Reactions of the laser vaporized SWNT depends upon defects induced by post-synthesis purification methods, the synthesis conditions should be optimized so that the impurities can be removed under the gentler conditions to avoid damaging the tubes. In this study, the effect of the laser pulse energy on the production of SWNT and the associated impurities were investigated. There is evidence to suggest that the carbonaceous impurities formed from long laser pulses are easier to remove than those impurities formed by short pulses. A comparison of SWNT samples resulting from laser vaporization at 1150 °C with short-pulses (8 ns, 1.06 μm), and long-pulses (a train of 80, 200-μs pulses, total length 200 μs, 1.06 μm) were investigated by Raman spectroscopy, TEM, FESEM, and microgravimetric analysis. The SWNT were then treated by a combination of chemical and/or thermal oxidation treatments and again characterized by the techniques described above. The results from this study will be presented, and the optimum conditions for production of SWNT for electronic applications will be discussed.

This research is sponsored by the U.S. Department of Energy and the Laboratory-Directed Research and Development Program at ORNL, under contract DE-AC05-84OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.


**W8.3**

**CARBON NANO-FLAKES GROWN BY MICROWAVE CVD**

Yihong Wu, National University of Singapore, Electrical and Computer Engg Dept, SINGAPORE.

Carbon nano-structures can be grown in a variety of forms such as nanos or buckytubes, nested spherical shells, giant fullerene shells, interconnected fullerene-like cages, and cross-linked graphitic cages. Here we report for the first time the growth of carbon nano-flakes aligned almost vertically to the substrate. The structure was found during the work on the growth of carbon nanotubes on different substrates by using a microwave CVD technique. The reaction gas is a mixture of hydrogen [80 SCCM] and methane [20 SCCM]. The typical process pressure and growth temperature are 1.7 Torr and 800°C, respectively. The growth of vertically aligned multilayer carbon nano-flakes were confirmed first on NiFs-covered substrates. The typical length of the nanoflakes is about 1 micrometer for a 5 minutes growth. The nanoflakes are separated from each other through they tend to form clusters. However, when switching over to substrate with other parameters and conditions remained unchanged, a totally different type of carbon nano-structure was formed which extends in a onion-like shape with a thickness of about 10-20 nanometers and the height of about 1 micrometer. The lateral dimension of the individual flakes is in the sub-μm range, and they are interconnected with each other along the substrate surface. FE-SEM observation revealed that some of them have “folded” tips, while some of them have an open top tip. For those with unfolded top tips, one side of the flakes tends to be covered with a layer of short nanoflakes or fibers. Good reproducibility has been obtained on substrates with different thicknesses of NiFs coatings, ranging from 20 to 100nm. Morphology and growth mechanism study and characterization of the structural and electric properties are in progress.

**W8.4**

**EFFECTS OF SILICON DOPING ON THE ELECTRONIC AND STRUCTURAL PROPERTIES OF CARBON NANOTUBES**

A. Pepezi, Antonio J.R. da Silva, Universidade de Sao Paulo, Instituto de Fisica de Sao Paulo, SP, BRAZIL; Conselho Nacional de Desenvolvimento Cientifico e Tecnologico, Brasilia, DF, BRAZIL; C. Figueiredo, Instituto de Fisica de Sao Paulo, SP, BRAZIL; E. Roncali, Universidade de Sao Paulo, Instituto de Fisica de Sao Paulo, SP, BRAZIL; J. Frisch, Universidade Federal de Santa Maria, Departamento de Fisica, Santa Maria, RS, BRAZIL.

The study of pure carbon nanotubes has been extremely active since their discovery by Iijima in the early 1990s, both from an experimental as well as a theoretical point of view. More recently, however, many devices having chemical compositions beyond that of pure carbon nanotubes have been proposed and experimentally realized. We present, for the first time, theoretical predictions of the electronic and structural properties of silicon doped carbon nanotubes, for different Si doping levels. All results are based on ab initio total energy calculations in the framework of the density-functional theory with the local density approximation. The Kohn-Sham equations are solved using a localized basis set and Troullier-Martins pseudopotential. The B3LYP functional is used to optimize the geometry of all the structures.

The B3LYP functional is used to optimize the geometry of all the structures.
eV/Å. As Si and C have the same number of valence electrons and a similar distribution of the outermost electrons in the free atoms, one would expect the Si defect to be rather inactive. However, we observe that there is an outward displacement of the Si atom, with a final Si-C bond length similar to what is observed in SiC. An analysis of the effects of the Si-impurity on the bond structure and density of states of both the metallic (6.0) and semiconducting (10.0) carbon nanotubes is presented. We show for the case of the (10.0) tube that, as a consequence of the geometrical distortions, Si produces an empty level in the gap which is highly localized on the Si impurity. Moreover, the highest occupied level also shows some degree of localization on the Si atom. For the metallic tube, we will analyze the changes produced by the impurity on the possible conducting channels, and discuss how this may affect the quantum conductance.

W9.5 DENSITY FUNCTIONAL THEORY STUDY OF SINGLE WALL CARBON NANOTUBES. Zhaqing Wang, Ruth Pechter, W. Wade Adcock, Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH; Braham Acklin, Ohio Supercomputing Center, Columbus, OH; Jean Blanche, Ohio Supercomputing Center, ASC/HP, Wright-Patterson AFB, OH.

We report a density functional theory (DFT) study of single wall carbon nanotubes with different diameters and chiralities. Carbon nanotubes are considered as periodic systems in the simulations. Comparative studies of DFT simulations using both atomic orbital and plane wave basis sets are discussed. Structural and mechanical properties, such as the Poisson ratio and Youngs modulus, in addition to vibrational frequencies, will be presented, as well as comparisons with other theoretical work and experimental data.

SESSION W9: POSTER SESSION
NANOTUBES, FULLERENES AND NANOSTRUCTURED CARBON: PROPERTIES AND APPLICATIONS
Chair: Rodney S. Ruoff and Vladimir I. Mekulov
Thursday, April 19, 2001
8:00 PM
Metropolitan Ballroom (Argent)


It is well known that carbon nanotubes and nanofibers exhibit exceptional field emitting properties. In order to utilize the full potential of carbon nanotubes/nanofibers, it is necessary to be able to synthesize them with defined diameters/radii. A new method is presented to grow nanotubes/nanofibers from a substrate (e.g. at emitter/pixel locations for a FED). This work examines the preferential growth of aligned carbon nanofibers by PECVD using lithographically patterned catalysts. In the PECVD deposition process, amorphous carbon will also be deposited together with the nanotubes. The challenge is to uniformly nucleate nanotubes and reduce the unwanted amorphous carbon on both the patterned and unpatterned areas. The structure/morphology of the catalyst (Ni and Co) plays an important role in the nucleation and uniformity of the nanofibers. A systematic study is performed by varying the structure of the catalyst and the PECVD growth parameters in order to obtain optimal growth conditions where nanotubes are only nucleated on areas with catalyst. Novel NEMS: Patterned growth of nanofibers by PECVD is demonstrated.

W9.2 Accepted. Withdrawn


A highly ordered alumina hole array which size is decreased down to 10nm was fabricated by anodic oxidation method. Carbon nanotube was grown vertically with thermal CVD at 700-850°C and analyzed by Raman and TEM. The contact resistance between carbon nanotube and the electrode decreased an order of magnitude by using rapid thermal annealing method. The contact resistance of the annealed samples are in the range of a few kΩ. The new structure of well defined electrical contact, which connects single carbon nanotube to metal electrode by using E-beam lithography is proposed. In this presentation, the relationship between carbon nanotube structure and the I-V characterization will be discussed.


We report structural studies of large-scale wurtzite GaN nanowires fabricated recently by direct reaction of Ga vapor and NH3. This recently reported growth technique [1] demonstrates processing of GaN on room-temperature substrates up to 26 nm and up to 500 μm in length. This method is both interesting and attractive in that fabrication is carried out without the assistance of template material as reported by other methods. In this study, transmission electron microscopy (TEM) is used to characterize the nanowires and to perform high resolution electron microscopy (HREM) and energy dispersive x-ray spectroscopy (EDS) data provide supporting structural/compositional analysis. Our structural investigation reveals the presence of short hexagonal plates, which are thought to play a critical role in the nucleation, growth, and orientation of the wires. In particular, our findings indicate the wires grow in the [210] direction or parallel to the hexagonal platelet edges. In addition, a growth mechanism is proposed based on the evidence presented in this study. [1] Miao He, I. Minus, P. Zuo, S.N. Mohammadi, Joshua B. Halpern, R.N. Jacobs, W.L. Surry, R.D. Valette and J. Salamone-Riba, Appl. Phys. Lett. (in press).

W9.5 LITHIUM INSERTION IN NANOPOROUS CARBON MATERIALS PRODUCED FROM CARBIDES. Lena Kosina, Victor Ledebe, Andrei Bies, Galen Paitzke, Zhuba Tikhonov, Petersburg Nuclear Physics Institute, Gatchina, Leningrad district, RUSSIA; Sergey Gordeev, Central Research Institute for Materials, St. Petersburg, RUSSIA; Thorgny Eelson, Skeleton Technologies Group, Stockholm, SWEDEN; Mariya Vayganskaya, Mechnikov Analyt Co, St. Petersburg, RUSSIA.

Lithium carbonylaceous materials have been the subject of intensive research and development for decades. It was shown that the structural variation of carbon materials plays an important role in a stoichiometry and a phase composition of the lithiated carbons. In this work, the results of a study of the process of lithium insertion in nanoporous carbons (NPC) produced from carbides (SiC, TiC, MoC) by chlorination are presented. These materials are of interest for their high developed surface (total porosity is up to 70%) on which lithium deposition can take place. Lithium insertion in the samples used in this study was carried by vacuum evaporation and subsequent diffusion at the temperatures ranging from 30°C to 200°C. After cooling lithiated samples were kept in an atmosphere of dry nitrogen. The nuclear reaction 7Li(p,n) He was used to measure the depth concentration profiles of lithium. Detailed analysis of the lithium concentration profiles showed that the process of lithium diffusion is strongly influenced by pore sizes and kinetics content. The profiles could be simulated by erfc function. It gave possibility to determine lithium diffusion coefficient (Dli). We determined Dli in the samples under study at various temperatures. Overall the largest values of Dli were obtained for n-porC, MoC-C, and the smallest for n-porC, SiC-C (for example, at temperature 100°C ~ 2510^-7 cm²/sec and ~ 4.0^-8 cm²/sec, respectively). It turned out that lithium diffusion coefficient does not stay constant for diffusion process. As a result of our experiment, it was elucidated that such behavior is connected with processes of diffusion on pores and intercalation of ordered graphite fragment going simultaneously. To investigate phase composition of the lithiated samples we used X-ray diffraction studies. Intercalation phases Li4C6, Li12C6, Li24C13 and Li40C24 were observed. Besides Li4C6 and Li24C13 phases were registrated in some cases. It was stated that the correlation between the diffusion rate and the evaporation rate is responsible for the phase composition. The reasons of this were analyzed and the conditions for producing of lithiated samples without lithium carbide and carbonate were found. The samples up to a thickness of about 0.6 mm uniformly impregnated by lithium and containing intercalation phases only were fabricated. The studies were carried out on NPC samples developed and produced in collaboration with Skeleton Technologies Group.

W9.6 Transferred to W6.7

W9.7 OXYGEN ION IRRADIATION OF LITHIUM-CONTAINING CARBON: IN SITU PHOTOELECTRON SPECTROSCOPY. Miriam Toner, Petra Benecke, Peter Oelhafen, Inst. für Physik, Univ. Basel, Basel, SWITZERLAND.
Lithium-containing carbon materials are studied with respect to various applications as oxygen gettering materials in thermonuclear fusion devices. Here, the behaviour of such materials under the conditions of oxidation and particle impact is of interest. In our experiments, amorphous carbon (a-C) thin films and polycrystalline graphite samples were used as host materials for the incorporation of lithium atoms. Either an a-C film was prepared or a polycrystalline graphite sample was introduced into the UHV-system and characterized with a-ray and ultraviolet photoelectron spectroscopy (XPS, UPS). Usually less than 10% of lithium were incorporated into the samples from a commercial source of lithium atoms. In further steps, monitored by XPS/UPS analysis without removing the samples from the vacuum, samples were exposed to oxygen at 500V to 3keV. At energies below 1.5keV, not the effect of ion impact, but of chemical oxidation dominated. The results with respect to chemical shifts and the segregation of lithium from the bulk were similar to those obtained after the exposure to molecular oxygen in earlier experiments. A new feature was the formation of lithium carbonate at the film surface. At higher energies, the physical impact of the ions became more important. Extended irradiation at 3keV induced further signal shifts and initiated the erosion of carbonate and oxide. This together with measurements on tilted samples supports the model of a layered structure of the oxidized films. Further irradiation at higher ion energies removed the lithium oxide and finally carbon itself and also initiated the formation of silicon oxide with the silicon of the film substrates. Control measurements were made on metal free carbon samples. Additional experiments were performed with hydrogen ions.

SESSION W10 POSTER SESSION DIAMOND-LIKE CARBON
Chairs: John W. Sollars and Richard B. Jackson
Thursday Evening, April 19, 2001
8:00 P.M. Metropolitan Ballroom (Argent)

W10.1 EFFECT OF SILVER INCORPORATION ON THE STRUCTURE, NANO-MECHANICAL PROPERTIES AND ELECTRICAL PROPERTIES OF TETRAHEDRAL AMORPHOUS CARBON THIN FILMS PREPARED BY PULSED LASER ABLATION. Q. Wei, J. Sankar, D. Kumar and J. Nirmayan, NSF Center for Advanced Materials and Smart Structures, Dept. Mechanical Engineering, NC A&T State University, Greensboro, NC.

We have prepared superhard amorphous carbon (a-C) thin films using pulsed laser ablation. To reduce the internal compressive stress and to improve the adhesion of the a-C films, we have incorporated compliant silver atoms into the growing a-C films by using an innovative and ingenious target design. The a-C films were characterized using visible Raman spectroscopy, nano-mechanical testing and transmission electron microscopy. It was found that the silver atoms did not cluster in the films. The a-C films containing silver exhibit significantly improved adhesion, while retain the superhard diamondlike properties. With this technique, relatively thick superhard a-C films can be prepared.


Tetrahedral amorphous carbon (t-C) has been studied with increasing interest for applications in the area of electronic and field emission devices, besides its widespread use in tribological applications. One of the main advantages of the hydrogen free diamond like carbon (DLC) or t-C is the possibility of tailoring the material with properties varying from diamond-like (sp^3) to graphite-like (sp^2) and to grow the material on different substrates at room temperatures. However, the high energy of the ions which leads to high sp^2 content in the films, could also be a problem, when growing the films on insulating or less conducting substrates. Under such conditions the films have been observed to have poor adhesion. Recently Arena et al. [1] have reported observing nanoclusters in the case of t-C films grown on aluminium. While the t-C films grown under identical conditions on silicon substrates were atomically smooth. Thus further indicating some dependence of the material properties on the substrate of the back contact. Hence, the effect of the back contact, a series of t-C films were deposited on silicon substrates with different metals for back contact. The back contact materials include tungsten, titanium, aluminium, chromium, copper, gold, and indium tin oxide on glass. Reported here is a comparison of the electrical and structural properties of the t-C films grown on different metal back contacts and Raman and XPS properties of the structural properties. The studies indicate that the back contact do influence the properties of the material to some extent. These results are analyzed with respect to an earlier report regarding, no significant influence of back contacts on field emission from similar t-C films [2].


W10.3 INTRODUCTION OF HYDROGEN AND OXYGEN INTO (t)-C CH THIN FILMS DEPOSITED USING DECR PLASMA. Fabrice Piaza, Centre de la Recherche Scientifique (CNRS), Laboratoire PHASE, Strasbourg, FRANCE; Dieter Grabmeier, Folker Herrmann, Forschungszentrum Rossendorf e.V., Institute for Isotopically Pure and Isotope Microscopy, Dresden, GERMANY; Gary Rehill, National Microelectronics Research Centre (NMRC), University College, Cork, IRELAND; Marie France Burthe, Pierre Desguerre, Centre National de la Recherche Scientifique (CNRS), Laboratoire CERI, Orleans, FRANCE; Andre Golanski, Centre National de la Recherche Scientifique (CNRS), Laboratoire PHASE, Strasbourg, FRANCE.

A distributed electron cyclotron resonance plasma reactor powered by a microwave generator operating at 2.45 GHz (800 W) was used to deposit (t)-C CH thin films at RT on single crystal Si substrates RF biased within the range 25<UB<600 V. Acetylene was used as a precursor. The plasma pressure was varied within the range 0.1<UB<1.5 mTorr. The films were analysed using Fourier transform infrared spectroscopy (FTIR). The nuclear reaction 1H+1H = 2H was used to determine the hydrogen content. At the plasma pressure of 0.1 mTorr both the growth rate V and the hydrogen concentration N_H remain constant (N_H ~20%) and V ~10%/(min) within the investigated bias range (25<UB<600 V). At higher pressures (P<0.1 mTorr) the growth rate increases linearly with the bias while the corresponding hydrogen content decreases at low bias and remains constant above U=150 V. Whist the pressure the probability of hydrogen incorporation is seen to increase with decreasing growth rate. At P<0.1 mTorr the FTIR analysis shows that the integrated intensity of the O-H band (3250-4000 cm^(-1)) remains constant within the bias range 0<UB<150 V. The corresponding intensity of the OH stretching band decreases with decreasing bias while the total hydrogen content increases, suggesting that molecular hydrogen may be present within the films grown at low bias. This result is tentatively correlated to the porosity observed within films deposited with U=80 V using positron Doppler broadening spectroscopy. Inspection of the GH stretching band shows that the nature of hydrogen bonding changes when substrate bias is varied while the integrated intensity of the OH band drops by almost an order of magnitude for the substrate bias higher than 150 V. This work has been funded in the framework of the European Community Biur-Burran Contract No BRPR-CT98-0749.

W10.4 DEPOSITION OF DIAMOND-LIKE CARBON FILMS BY ELECTROLYSIS OF ACETYLENE-AMMONIA SOLUTION. Andrei M. Mysev, Inst of Solid State and Semiconductor Physics, Minsk, BELARUS; Patrice Angelov, Inst National Polytechnique de Grenoble, MGLP, Grenoble, France; Andrei Genin, Inst of Solid State and Semiconductor Physics, Minsk, BELARUS; Irina Fomicheva, Tatiana Kuznecev, Inst of Powder Metallurgy, Minsk, BELARUS.

Synthesis of carbon by electrolysis of acetylene-ammonia solution with Ni and Si electrodes has been studied. An acetylene solution in liquid ammonia of 15 mol. % was used as electrolyte. Nickel foils and n-type >10^6 Ohm-cm Si plates were used as substrates. A.c. voltage of 2-150 V was applied over 2-10 hours. Experimental details are described elsewhere [1]. Carbon films were obtained on the cathode at applied voltages higher than 30 V. This voltage was used for the anode. The films exhibited different crystallinity and different sp^3/sp^2 ratio depending on the cathode material (Ni or Si). Electron diffraction (ED) from the film obtained on the Ni cathode gave two broad rings. Calculated lattice parameters are a=2.03 nm and c=2.016 nm which are close to those of graphite 4 H (ASTM No 25-384). ED from the film synthesized on the Si cathode exhibited rings and diffuse halo. Calculated d (nm) values are 1.027±1, 1.034±1, 1.060±1, 1.80±2. The best assignemnt of this ED pattern among all known carbon phases was achieved for a cubic lattice with a cell dimension a=0.354±1 nm. Raman spectrum of the film synthesized on the Ni cathode demonstrated three broad bands with maximum at 1340, 1460 and 1600 cm^-1. This spectrum is characteristic for a graphitic phase with some fraction of sp^3 bonded carbon. Raman spectrum of the film obtained on the Si-cathode demonstrated a weak
peak at ~1310 cm⁻¹ and three broad bands: 1150-1350 cm⁻¹, 1400-1500 cm⁻¹, and 1600-1700 cm⁻¹. This spectrum was attributed to the presence of Si-C and Si-H bonds, and high-resolution Si spectra have been discussed. It was proposed that synthesis of carbon occurs through dehydrogenation and polymerization of acetylene caused by atomic hydrogen generated on the cathode from reduction of ammonia ions.

L.T. McIntyre, V.V. Novikov, L.L. Klinskovich, Y. Bandh, Carbon, October 20, 2000.

W10.5 PREPARATION AND PROPERTIES OF AMORPHOUS CARBON OXYNITRIDES a-C:N-Oₓ FILMS MADE BY A NITROGEN RADICAL SPATTER METHOD AND BY THE LAYER-BY-LAYER METHOD. Yutaka Naruse, Shoji Nitta and Hitoshi Habeuchi. Department of Electrical Engineering, Tokyo Institute of Technology, Gifu, JAPAN. *Gifu National College of Technology, Gifu, JAPAN.

We have prepared very interesting amorphous carbon nitride a-C:Nₓ films by a nitrogen radical sputter method. With atomic hydrogen treatment of a-C:Nₓ, we have obtained good electronic properties with fewer defects. We have used the cyclic process of the deposition of a-C:Nₓ by a nitrogen radical sputter and of the etching by hydrogen plasma and obtained the layer-by-layer LS LS, a-C:Nₓ with good electronic properties. In this paper, the effect of oxygen plasma on a-C:Nₓ was studied. It is not possible to get a oxidized carbon nitride film by introducing both of nitrogen and oxygen as spatter gases. It is confirmed that the oxygen plasma has three effects on a-C:Nₓ. One is an etching of a-C:Nₓ, decreasing the film thickness. The other is to oxidize a-C:Nₓ, and producing amorphous carbon oxynitride a-C:N-Oₓ films. The third one is the formation of pair defect states in a-C:Nₓ and decreases defect density. The occurrence of these three depend on the preparation conditions. a-C:N-Oₓ films show higher optical gaps and smaller defect densities from experiments on XPS, optical transmission spectra, photothermal deflection spectra and ESR. These refinements of the electronic properties increase photoluminescence PL spectra up to 3.5 eV and especially the intensity at ultraviolet region of PL. The oxygen plasma treatment seems to change a-C:Nₓ to more porous a-C:N-Oₓ. These two properties are good for applications of a-C:N-Oₓ to luminescent materials and also as a low dielectric constant materials. We have studied the deposition of a-C:Nₓ on a-C:N-Oₓ. A-C:N-Oₓ deposited on a-C:Nₓ contains defects. This was confirmed by the layer-by-layer amorphous carbon oxynitride LS LS, a-C:N-Oₓ with a cyclic process of the deposition of ultra thin a-C:Nₓ by a nitrogen radical sputter method and of the etching by the oxygen plasma treatment.

W10.6 HARD CARBON FILMS CONTAINING TITANIUM AND BORON CARBIDE. Ayako Kimura, Yasushi Azuma, Kunihito Yamada, Tetsuya Safarame, Kent Uchi, Dept. of Mechanical Engineering, Yokohama, JAPAN.

Ceramics thin films such as TiN, TiC and [TiAl]N synthesized by the cathodic arc-discharge method have excellent hardness, density and adhesion strength. Therefore, many researches have recently been reported on synthesizing hard carbon films by this method using carbon cathodes as raw materials. The obstacle of using carbon cathodes lies in the difficulty to control the deposition rate, presumably due to lack of electrical conductivity of carbon cathode compared with metals and alloys. For example, the carbon surface would not be uniformly arc-discharged and many macrostructures are emitted from the carbon cathode. As a result, the surface of films is contaminated with these macrostructures and becomes very rough. In order to solve the above problem, we focused on controlling the macrostructure and electrical conductivity of the carbon cathodes by the addition of conductive powder during the sintering of carbon, C, Ti and B powders were mixed and sintered by the hot-pressing method under 15 MPa at 2200°C. In this experiment, Ti atomic ratio against C and B was changed to seek the best cathode characteristics and density of arc-discharge. Furthermore, pyrolytic and natural carbon were also used as cathodes for comparison. Using these cathodes, hard carbon films with Ti, B and their compounds were synthesized on WC-Co and Si substrates by arc discharge method. In this paper, we report that surface roughness and adhesion strength of hard carbon films could be improved by controlling microstructure of macrostructures by arc-discharged carbon cathodes.

W10.7 PARAMAGNETIC CENTERS IN AMORPHOUS CARBON-BASED THIN FILMS. Malek Tahvild, Theodore Christidis, Sanith Janber, Dept. of Physics, University of Toronto, 80 St. George St., My All Ek-Hilkhani, Philippe Napol, Mohamed Chaker, INRS-Energie et Matériaux, Varennes, CANADA.

In this work, Electron Paramagnetic Resonance (EPR) is used to study paramagnetic centers in unhydrogenated amorphous carbon based thin films, namely Diamond-Like Carbon (DLC), amorphous silicon carbide (a-SiC) and carbon nitride (a-CNx) thin films. DLC and a-CNx films were deposited using a KrF excimer laser, while the a-SiC films were synthesized using the same technique combined with a nitrogen surface wave plasma. For all three types of films, the spin density was found to be of the order of 10¹⁸ cm⁻³ and the deactivation is due to temperature and laser intensity. Also the g-value of the EPR signal was measured to be close to 2.0028 and the EPR lineshapes were found to be dominantly Lorentzian. These observations indicate that the paramagnetic centers in these films are most probably centered sp³ carbon related defects leading to an exchange narrowed EPR temperature linewidth ranging from 3.2 to 8 Gauss. The thermal dependence of the EPR linewidth is also investigated and discussed in terms of the conduction mechanisms in these films. The increase of the EPR linewidth with temperature is attributed to spin hopping between neighboring sp³ clusters that appears to be an important conduction mechanism, especially at temperature ranging from 20 to 100°C. For the DLC films, the EPR linewidth was found to increase with laser intensity, while for the a-CNx films, an increase in nitrogen incorporation [17 to 25%] is detected for a narrowing of the EPR line. This latter effect could be explained by the occurrence of nitrogen bridging between adjacent paramagnetic centers leading to larger clusters of aromatic rings are formed. The conductivity measurements and the thermal dependence of the EPR linewidth are explained within such a model of nitrogen incorporation in DLC.

W10.8 FIRST- AND SECOND-ORDER RAMAN SCATTERING SPECTRA OF CARBIDE CLUSTERS IN NANOPOROUS CARBON PRODUCED FROM CARBIDE MATERIALS. A.M. Danilichkivski, S.K. Gordeev, A.V. Grechinskaya, N. Ektarynov, T. Khotyn, V. Grechinskaya, I. Technical Institute, St. Petersburg, RUSSIA. 3 Central Science Research Institute for Materials, St. Petersburg, RUSSIA. 4 Skeleton Technology Group, Stockholm, SWEDEN.

In this work Raman scattering from nanoporous bulk carbon (np-C) samples produced from polycrystalline silicon and molybdenum carbides by chemical reaction with chlorine at 800°C is investigated. np-C materials with porosity up to 70% has attractive physical and chemical properties which can be controlled over some limits by variation of initial composition and they are of considerable promise for applications. Structures of the np-C materials have been studied by small angle X-ray scattering (SAXS [1-3] and valence bonds by X-ray photoelectron spectroscopy (XPS) [4]. There was shown that the np-C materials exhibited a high degree of size homogeneity of nanoparticles (probably, they are pores) with typical dimensions 1-20Å, depending on the type of initial carbide, responsible for SAXS characteristics. Orthogonal scattering configuration and different polarizations of incident and scattered light beams were used in Raman measurements. The scattering was excited by lines of argon or krypton lasers. It can be seen from Raman spectra of first order that well known for disordered graphite carbons wide G and D bands have rather complex structure for np-C materials and their position are shifted from usual values. For example, G band maximum is localized near 1600-1602 cm⁻¹ on frequent occasions Raman spectra for np-C samples produced from varied carbides are different. Both of wide bands undergo shifts in the exciting light source from 637 μm with considerably more changes for D-band. Spectral band shapes are changed markedly with the altering of polarization configuration. Several not too narrow bands were observed in the frequency range 40 - 150 cm⁻¹. Their position do not coincide with those bands of water, oxygen or nitrogen which could be absorbed on pore walls. It is felt that some of them are breathing modes of hollow clusters. Interesting features were observed in the second order spectra. Raman modes observed for np-C samples in distinct polarization configurations differ significantly in frequency from two-phonon modes known for microcrystalline graphite [5]. They substantially depend on polarization configuration and are also dissimilar for different np-C materials. At present model of the microstructure and fragment structure underlying of the carbon clusters in these materials.

The studies were carried out on NPC samples developed and produced in collaboration with Skeleton Technologies Group. This research was fulfilled with the support of RFBR (95-02-17884) and Swedish Research Council (VR-1999-0141, N5, p. 888).

amorphous diamond makes these mechanical devices particularly interesting. These properties include the existence of a two-phase microstructure, described as interpenetrating nanophases of 50% and 33% or 50% diamond, which enables plastic-like mechanical deformation of the material. This property allows the residual strain in the films to be reduced below 0.0001 - a critical requirement for thin-film micro-electromechanical systems. Owing to its very high elastic modulus, approaching 800 GPa, and high fracture strength, ~8 GPa, the strong high permits ultra-thin free-standing membranes of amorphous diamond to be synthesized (0.1 micron thick), and we describe a vibrational mode in these membranes (5 GPa) as a chemical sensor. Lastly, the material is chemically inert and biologically compatible as tested through in vivo cell adhesion studies, which should enable future bioMEMS structures.

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


Nanostructured carbon consists of highly disordered clusters of graphene-like structures. The degree of bonding disorder and morphological richness are controlled by the energetic film growth. These films grow at room temperature and have negligible film stress, meaning that they can grow on any substrate to any desired thickness. We have studied films of nanostructured carbon with various morphologies for acoustic and piezoelectric properties in surface-wave transducers to be used in microsensors. Many of the nanogray state test have response sensitivities greater than an order of magnitude over conventional materials. Intriguingly, the sensor response is not a function of the angle of the source or its position. Instead, the sensor is a function of the frequency of the material and the thickness of the film, with a particular graphhene-bonding character. We will present nanostructural and chemical bonding properties from nanostructured carbon films and function of growth energetics and correlate these properties to microsensor sensitivities. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. DOE under Contract DE-AC04-94AL85000.

9:45 AM *W11.4* X-ray reflectivity measurement of ultra-thin diamond-like carbon coatings for magnetic hard disk drive applications. A. Liebass, B.K. Tanner, Dept. of Physics, Durham University, Durham, UNITED KINGDOM; A.C. Ferrari and J. Robertson, Engineering Dept, Cambridge University, Cambridge, UNITED KINGDOM.

X-ray reflectivity (XRR) has been employed to investigate ultra-thin films of tetrahedral amorphous carbon (ta-C) grown on magnetic recording media. ta-C (~50-100 nm) has been deposited by electron cyclotron resonance (ECR) and deposition is performed at (~200 °C). The growth is monitored using high resolution XRR. The films have been deposited on magnetic heads in situ using a variety of sputter deposition techniques. The films exhibit a range of thicknesses and compositions, and the effects of substrate temperature on the film properties are examined. The reflectivity is measured as a function of scattering vector, and the results are compared to theoretical calculations. The results are then used to predict the performance of the magnetic recording media. The reflectivity is measured as a function of scattering vector, and the results are compared to theoretical calculations. The results are then used to predict the performance of the magnetic recording media. The reflectivity is measured as a function of scattering vector, and the results are compared to theoretical calculations. The results are then used to predict the performance of the magnetic recording media.
11:00 AM W11.8
ELASTIC CONSTANTS OF NANOMETER THICK DIAMOND-LIKE CARBON FILMS
Marco G. Beghi, Carlo E. Bottini, Andrea Di Brasi, Roberta Pastorelli, Politecnico di Milano, Dept. of Nuclear Engineering, Milano, ITALY; Andrea C. Ferrari, John Robertson, Cambridge University, Engineering Dept., Cambridge, UNITED KINGDOM.
Carbon films of thickness down to 2.5 nm are necessary to achieve a storage density of 100 Gbit/in² in magnetic hard disks. Reliable methods to measure the properties of these ultrathin films, especially in the case of hard films with amorphous carbon-like structures, have to be developed. We show for the first time that combining Surface Brillouin Scattering (SBS) and X-ray reflectivity measurements the elastic constants of such films can be obtained. Tetrahedral amorphous carbon films were deposited on Si, by an S bend filtered cathodic vacuum arc, which provides a continuous coverage on large areas free of macroparticles. Films of thickness down to 3 nm were produced and characterised. Film thickness and mass density are measured by X-ray reflectivity, densities in excess of 3 g/cm³ are found, indicating a significant sp³ content. Measurements also give evidence of a grading of film properties, the density declining in the neighbourhood of the external and internal surfaces. The dispersion relations of surface acoustic waves are measured by SBS for films of different thickness and for the bare substrate. We show how waves are still well described by a continuum elastic model, which uses a single homogeneous equivalent film. Fitting of the dispersion relations, computed for given film properties, to the measured dispersion relations allows the derivation of the elastic constants. For a 8 nm thick film we find a Young's modulus E around 480 GPa, with a shear modulus G lying in the 140-260 GPa interval. For a 3 nm thick film, E is around 320 GPa, with G lying in the 100-180 GPa interval, due to the higher influence of the lower densities interfaces. These are the thinnest films of any material for which a direct measurement of the elastic constants have been reported. A detailed study of how the growth and characteristic nanometer size tetrahedral amorphous carbon films, which maintain their extraordinary density and mechanical properties down to the nm range, and thus satisfy the requirements set for the ideal hard disk coating material.
Hydrogen-free amorphous diamond-like carbon films have stimulated great interest owing to the unique properties of these materials. Amorphous carbon films prepared by different chemical vapor deposition processes have shown promising optical, electrical, and mechanical properties. These properties make diamond-like carbon films suitable for a wide range of applications, including coatings, lubricants, and electronic devices.

1:45 PM W12.2
NANO-STRUCTURED AMORPHOUS CARBON FILMS SYNTHESIZED USING DECIR PLASMA. Andrei Golinski, Philippe Kern, Fabrice Piazza, Jean-Paul Stoquert, Centre National de la Recherche Scientifique (CNRS), Dept. PHASE, Strasbourg, FRANCE. Jean Hamel, Centre National de la Recherche Scientifique (CNRS), Dept. IPCMS, Strasbourg, FRANCE. Liam McDowell, Centre for Surface and Interface Analysis, Dept. of Applied Physics and Instrumentation, Cork Institute of Technology, Cork, IRELAND. Deter Grundmann, Forschungszentrum Rossendorf e.V., Institut für Innere Strahlenphysik und Materialforsehung, Dresden, GERMANY.

Diamond-like amorphous carbon (DLC) films were deposited on single crystal Si substrates at RT using a plasma source operating in a Distributed Electron Cyclotron Resonance (DECR) configuration. The microwave frequency applied in the frequency range of 3.45 GHz was applied to several substrates located in the vicinity of the reactor walls equipped with magnetic racetracks designed to provide an appropriate confinement of fast electrons. The plasma chamber was equipped with a graphite sputtering target biased by a pulsed DC power supply producing negative high voltage of tunable amplitude. The substrate bias was regulated using an RF power supply operating at 13.5 MHz. The DLC films investigated using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), nuclear reaction analysis (NRA) using the resonance at 6.385 MeV of the reaction: $^{15}$N + $^{1}$H $\rightarrow ^{14}$C + $^{4}$He, elastic recoil detection analysis (ERDA) and Rutherford backscattering (RBS). For the films deposited at the plasma pressure of 0.3 mTorr and substrate bias of -80 V the AFM and XPS analysis reveal the presence of basket-like clusters of circular hillocks 20 nm high surrounded by a planar, mostly sp$^2$ bonded film $\sim$8 nm thick. With increasing plasma pressure the distribution of the hillocks becomes more homogenous and more clusters of the basket-like cluster formation decreases significantly. The XPS data taken at decreasing energy show that the structure of the hillocks is dominated by sp$^3$ bonded carbon. The XPS carbon signal disappeared at $\sim$10$^\circ$ energy angle indicating that integration of argon occurs mainly within the sp$^3$ bonded regions. The NRA, ERDA and RBS measurements show that the hydrogen content increases with decreasing substrate current density while argon integration is enhanced by increasing bias.

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2:00 PM W12.3
COMPARISON OF CPM, PDS AND OPTICAL TRANSMITTANCE OF AMORPHOUS CARBON NITRIDE FILMS MADE BY A NITROGEN RADICAL SPUTTER METHOD. T. Kusaba, S. Naka and H. Hada, Dept. of Electrical Engineering, Gifu University, Gifu, JAPAN. *Dept. of Electrical Engineering, Gifu National College of Technology, Motou, Gifu, JAPAN.

The constant photocurrent method (CPM), photothermal deflection spectroscopy (PDS) and optical transmittance are used to obtain the information near the optical band gap and defect densities. A-CN films have high resistivity, so it is difficult to obtain photocurrent. But photothermal deflection spectroscopy and the two-layer method have high photocurrent, so the absorption coefficient can increase. Spectra of CPM and CPM spectra at high photon energy region - are obtained by dc measurements. We prepared a-CN made by a nitrogen radical sputtering method and by the two-layer method and high photocurrent. Using a nitrides material, a spectra of CPM and CPM spectra at high photon energy region are obtained. A-CN films have high resistivity, so it is difficult to obtain photocurrent. But photothermal deflection spectroscopy (PDS) and optical transmittance are used to obtain the information near the optical band gap and defect densities.
Tokyo, JAPAN; CREST, Japan Science and Technology Corporation (JST), JAPAN.

The nanoscale separation of H-terminated area and O-terminated area on diamond surface is very attractive for carbon nano technology. Because the H-terminated diamond surface shows p-type conduction, negative electron affinity and hydrophilicity. On the other hand, O-terminated diamond surface exhibits insulating, positive electron affinity and hydrophobicity. Both surfaces are stable in the air and the properties maintain for a long time. This characteristic is specific to diamond surface and it has a potential to pioneer surface properties utilization. The prototype nano electron devices have been demonstrated [1] [2] using the local oxidation on the hydrogen-terminated diamond (101) surface by atomic force microscopy (AFM).

In this study, we have investigated the mechanism of surface local oxidation of diamond. The diamond surface is scanned with tip-to-sample bias in the moisture-controlled air. Under proper conditions, the diamond surface can be oxidized with a line with 3nm in width is obtained using the tip coated with W/C. The reaction occurs only when the sample surface is positively biased with respect to the AFM tip. We performed local oxidation in the relative humidity (20-60%) and the fact that the water layer on the surface is necessary for the oxidation has been interpreted by Sugimura et al. [3], so the AFM oxidation process is analogous to the electrochemical anodic oxidation in which the sample acts as anode while the AFM tip acts as a cathode and water layer from the ambient on the sample surface acts as electrolyte. We also applied AC bias modulation to oxidation process and significant enhancement of line width was achieved. Using this AC bias oxidation process on the hydrogen-terminated diamond surface, we can create a new nanoscale technology based on diamond.


3:30 PM W12.7
RAMAN AND EELS STUDIES ON MICROCRYSTALLINE DIAMOND PREPARED IN A LOW PRESSURE INDUCTIVELY COUPLED PLASMA. Katsuyuki Oikawa, Shinsuke Komuro, Seichiro Matsunoto, National Institute for Research in Inorganic Materials, Tsukuba, JAPAN.

Micronicrystalllne diamonds with several hundred nm in diameter have been prepared in a 13.56 MHz low pressure inductively coupled CH₄/H₂ or CH₄/CO/H₂ plasma. The bonding structures were investigated by Raman spectroscopy and electron energy loss spectroscopy (EELS). Visible (514 nm) and UV (395, 344 nm) excited Raman spectra exhibit peaks at around 1150 cm⁻¹ assigned to sp³ bonding and at 1332 cm⁻¹ due to zone center optical phonon mode of diamond respectively [1]. It indicates that the UV excitations are possibly sufficient to induce the sp² bonding on the surface of sp³ bonded carbon. The high resolution EELS spectra show peaks at around 1100 cm⁻¹ assigned to C=C stretching vibration of sp³ bonding and at 700 cm⁻¹ corresponding to the bending vibration of sp²-C=C-C(sp³). It is qualitatively in agreement with the Raman spectra. Furthermore the quantitative analysis of sp² and sp³ bonding is carried out by comparing the peak area of 285 eV with the signal area at around 291 eV in the EELS spectra [1].


3:45 PM W12.8
THE EFFECT OF NITROGEN INCORPORATION ON THE NANOSTRUCTURE OF ULTRANANOCRYSTALLINE DIAMOND THIN FILMS. James Birrell, University of Illinois, Dept of Materials Science, Urbana, IL; J. Murray Gibson, Dieter Gruen, Orlando Asciello, John Carlisle, Somnath Bhattacharyya, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Ultrananocrystalline diamond (UNCD) thin films grown via microwave plasma chemical vapor deposition using CH₄-Ar-N₂ gas mixtures with increasing N₂ content exhibit increasing conductivity from about 10⁻³ (Ω cm)⁻¹ to 0.150 (Ω cm)⁻¹ for films grown with 1% to 20% nitrogen in the plasma. The effect of nitrogen incorporation on the morphology of UNCD films has been studied using High Resolution Electron Microscopy (HREM), electron diffraction, and EELS. It is found that as the nitrogen content of the plasma is increased up to 20%, the grain size and the grain boundary width increases. This trend reverses when 20% N₂ or more is used. EELS and electron diffraction confirm that the grain boundaries in the UNCD thin films are phase boundaries and show a structure similar to amorphous carbon. Neither the grains or the grain boundaries show detectable nitrogen incorporation, although EELS data indicate that the films contain up to 3% atomic % nitrogen. The group also investigated the effect of nitrogen incorporation on diamond thin film conductivity. From these studies, it is believed that the change in the nanostructure of these films heavily influences their conductivity and electron emission properties.

4:00 PM W12.9
STUDIES OF MECHANICAL PROPERTIES OF ULTRA NANOCRYSTALLINE DIAMOND (UNCD) THIN FILMS USING NANOINDENTATION. A.V. Singaram, O. Auers, D.M. Greve, J. Birrell and J.A. Carlisle, Materials Science Division, Argonne National Laboratory, Argonne, IL; H.D. Espinosa and D.C. Proctor, Department of Mechanical Engineering, Evanston, IL.

Over the past few years, there has been rapid growth in the use of UNCD technology. The applications based on UNCD technology are evolving so rapidly and in so many diverse areas that there are ever increasing demands on the limits of UNCD devices, which have triggered the search for new materials having superior physical, chemical, and mechanical properties. As far as the mechanical properties are concerned, future UNCD devices may involve significant bending, rolling, and sliding contacts. Therefore, there exists an immediate need to develop a material with excellent mechanical properties as well as studying these properties at the micro/nano scale. Diamond is known for its outstanding mechanical properties; however, diamond coatings grown by conventional chemical vapor deposition (CVD) methods exhibit coarse-grained microstructures (RMS roughness ~ 0.5 μm) that prevent fabrication of ultrananocrystalline diamond (UNCD) coating technology developed at Argonne National Laboratory that offers a unique way of producing phase-pure diamond with extremely smooth surfaces (RMS roughness ~ 34 nm). In this paper, we will discuss detailed studies of the mechanical properties of UNCD coatings grown with and without nitrogen (N₂) incorporation by nanoindentation. The results are discussed in terms of the change in the mechanical properties of UNCD coatings with changes in microstructure and grain boundary structure induced by nitrogen incorporation.


4:15 PM W12.10
NANOSTRUCTURED DIAMOND THIN FILMS ON Co-Cr-Mo WITH TiN INTERLAYERS FOR BIOMEDICAL IMPLANT PURPOSES. Marc D. Bies and Yogesh K. Vohra, Department of Physics, University of Alabama at Birmingham, Birmingham, AL, USA.

Work is progressing on deposition of diamond thin films on human artificial joint implants in order to extend their service lifetimes, which are currently around 10 years long. The predominant failure mode of these implants involves corrosion of metallic wear surfaces and subsequent degradation of adjacent polymer components. To prevent this, nanocrystalline diamond thin films are deposited on the metal articulating surfaces to protect against both chemical attack and mechanical abrasion. The Co-Cr-Mo alloy that comprises most implant joints resists diamond thin film growth by catalytic degradation during deposition, producing films predominantly composed of graphite and amorphous carbon. To prevent this interaction, a layer of TiN has been deposited on the Co-Cr-Mo surface with the TiN serving as a diffusion barrier during deposition. TiN is well suited to its hardness, good biocompatibility, low permeability to carbon, and it is proven as a good substrate for diamond deposition. Complete films will be tested by XRD and Raman spectroscopy to determine diamond content, AFM to determine surface roughness. Rockwell indentation to determine adhesion strength, and nanoindentation to determine film hardness.

This work was supported in part by the Alabama Space Grant Consortium under NASA Training Grant NGT-15-40018.

4:30 PM W12.11
DENSITY-FUNCTIONAL BASED TIGHT BINDING STUDY OF C₂ AND CN DEPOSITION ON THE (100) DIAMOND SURFACE. Michael Sternberg, Thomas Fraenkel, Department of Physics, University of Paderborn, Paderborn, GERMANY; Peter Zapf, Larry A. Curtiss, Dieter M. Greve, Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL.

A density-functional based tight binding method was used to study elementary steps in the growth of ultrananocrystalline (UNCD) diamond. It was shown previously that C₂ dimers are the dominant growth species in hydrogen-poor argon plasma. Recent experimental evidence shows that nitrogen addition to the plasma profoundly changes the morphology of UNCD film. C₂ dimers are believed to play a major role in this case. Reactions of these molecules with undecorated and monohydrided reconstructed diamond (100) surfaces were studied. A diamond growth mechanism by direct insertion of C₂ dimers into dimer rows on the substrate is proposed. For simplicity, we consider two dimer rows on the substrate. The single CN prefers a one end attachment to a surface atom with its C.
end down on the unhydrated (100) surface. Stable structures of the
adsorbates and reaction energies are determined. The adsorption
energies are consistently exothermic. Diffusion barriers and pathways
are discussed. Reactions between adsorbate molecules can lead to
growth and also to nucleation of new diamond crystallites.
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