

SYMPOSIUM W

Nanotubes, Fullerenes, Nanostructured and Disordered Carbon

April 17 – 20, 2001

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* Invited paper

SESSION W1: FULLERENES

Chairs: David B. Geoghegan and David E. Luzzi
Tuesday Morning, April 17, 2001
Metropolitan I (Argent)

8:30 AM *W1.1

CRYSTALLOGRAPHIC STUDIES OF ENDOHEDRAL FULLERENES, FULLERENE/PORPHYRIN C₆₀-CRYSTALS AND FULLERENE DIMERS. Alan Balch, Marilyn M. Olmstead, Ana de Bettencourt-Dias, Pam Lord, Univ of California, Dept of Chemistry, Davis CA; Harry C. Dorn, Steve Stevenson, Virginia Technical Univ, Dept of Chemistry, Blacksburg VA; Glenn Miller, Univ of New Hampshire, Department of Chemistry, Durham, NH.

Recent advances in obtaining ordered crystalline forms of various fullerenes (including endohedral fullerenes such as Sc₃N@C₇₈, fullerene/porphyrin aggregates, and covalent assemblies with more than one fullerene) 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, 7090. This talk will present recent structural work in this area.

9:00 AM *W1.2

PUTTING FULLERENES AND METALLOFULLERENES INTO CARBON NANOTUBES. Toshiya Okazaki, Nagoya Univ, Dept of Chemistry, Nagoya, JAPAN; Kazutomo Suenaga, Kaori Hirahara, Shunji Bandow, Sumio Iijima, Japan Science and Technology Corporation, c/o Meijo Univ, Dept of Physics, Nagoya, JAPAN; Hisanori Shinohara, Nagoya Univ, Dept of Chemistry, Nagoya, JAPAN.

We report the high-yield synthesis for various empty fullerenes (C₆₀-C₉₀) and endohedral Gd, Sc, Sm metallofullerenes containing SWNTs through the vapor phase reaction and the spectroscopic characterization of the encapsulated metal atom ion by using the electron energy-loss spectroscopy (EELS). For example, the obtained EELS spectra reveals that the encapsulated Sm ion takes 2 state in (Sm@C₈₂(I))_n@SWNTs irrespective of the physical and the electronic properties of SWNTs. During the electron beam irradiation, the divalent Sm²⁺ spectrum is gradually converted to that of the trivalent Sm³⁺. At the same time scale, the coalescence of the Sm@C₈₂(I) molecules within the SWNTs is observed by the high-resolution transmission electron microscopy (HRTEM).

9:30 AM W1.3

ENCAPSULATED MOLECULES IN CARBON NANOTUBES: STRUCTURE AND PROPERTIES. Richard Russo, Brian W. Smith, S.B. Chikkannanavar, D.E. Luzzi, University of Pennsylvania, Dept of MS&E, Philadelphia, PA.

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 C₆₀ as well as other higher order fullerenes and metallofullerenes such as La₂@C₈₀ and Sc₃N@C₈₀. The structural properties of these nanoscopic 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 length 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 1-D 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 non-confined 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 La₂@C₈₀ is consistent with the electronic structure (La³⁺)₂@C₈₀⁶⁻ 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.

9:45 AM W1.4

BLOWING UP A NANOBALLOON: A HOLLOW AMORPHOUS BORON BALL COATED WITH CRYSTALLINE BORON NITRIDE

ON BOTH INTERIOR AND EXTERIOR SURFACES.

Shojiro Komatsu, NIRIM, JAPAN; Yoshiki Shimizu, Yusuke Moriyoshi, Hosei Univ, JAPAN; Katsuyuki Okada, Mamoru Mitomo, NIRIM, JAPAN.

Hollow nanoparticles of amorphous boron coated with crystalline boron nitride on both the interior and exterior surfaces have been synthesized. The typical diameter and the thickness of the "balloon" wall were about 200 nm and 30 nm, respectively. The method was a pulsed-laser-vaporization of boron nitride with the assistance of modulated plasma jet, that was synchronized with the laser-pulsation. We suppose that a tiny liquid droplet produced by intense laser irradiation of BN was blown up into a nanoballoon by a blow of plasma jet, owing to the synchronization of the modulated plasma jet and the laser pulsation.

10:30 AM W1.5

EXTERNAL CHEMICAL REACTIVITY OF FULLERENES AND NANOTUBES. Seongjun Park, Stanford University, Dept of Chemical Engineering, Stanford, CA; Deepak Srivastava, NASA Ames Research Ctr, Nanotechnology at CSC/NAS, Moffett Field, CA; Kyeongjae Cho, Stanford Univ, Dept of Mechanical Engr, Stanford, CA.

Fullerenes and nanotubes have been considered as promising materials for nanotechnology. Since attaching external atoms or molecules functionalizes fullerenes and nanotubes in most of their applications, there are increasing interests in the ways to control the local chemical reactivity. [1] In general, the chemical reactivity is characterized by the pyramidalization of carbon atoms. [2] The pyramidalization rehybridizes carbon atomic orbitals of fullerenes and nanotubes between *sp*² and *sp*³ rather than *sp*² in graphite. There are two factors controlling the chemical reactivity, which are the strain energy for pyramidalization and the occupancy of s orbital in π state. We analyze those factors using elastic strain energy analysis and POVA (π orbital vector analysis) [2], respectively. And we developed an analytic and quantitative framework to predict the chemical reactivity. In order to verify the idea, we applied the idea to the hydrogenation of graphite and different fullerenes and nanotubes to gauge the role of three different dimensional structures: fullerenes are for 3-D structure, nanotubes are for 1-D structure and graphite is for 2-D structure. All the calculations are performed using total energy pseudo-potential density functional theory [3], and we have obtained excellent agreements between the proposed framework and full DFT calculations.

1. Srivastava, D. et al. *Journal of Physical Chemistry B* **103** 4330 (1999).
2. Haddan, R.C., *Science* **261**, 1545 (1993).
3. Payne, M.C., et al. *Reviews of Modern Physics*, **64** (4) 1045 (1992).

10:45 AM W1.6

C₆₀ CLUSTERS SELF-ASSEMBLY IN ONE-BEAM OPTICAL TRAP. W. Eugene Collins, Don Henderson, Weijie Lu, Andrey Zavalin, Fisk Univ, Physics Dept, 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 microbiology techniques. Contribution of optical trapping to nano-technologies promise to be more significant. Previous experiments in optical trapping showed trapped particles creating quasi-molecular symmetric dynamic structures, assembled together by photons and existing only in presence of laser field. Under the certain conditions photon bonding C₆₀-C₆₀ 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 μm-optical cell, filled by C₆₀/toluene solution. C₆₀ clusters were created on the glass surface and in the volume of solution, maximum up to 20 μm size. It was possible to grow stable structures in different shape (lines, rods etc.) by motion of optical trap along surface of substrate and z-axis of laser beam. Parameters of photon and chemical bonding were measured during process of growth by spectroscopy in laser trap. C₆₀ cluster size was measured by 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 report experimental spectra and AFM-images are presented and models of transition from photon bonding to chemical bonding are discussed.

11:00 AM W1.7

TRANSITION TEMPERATURE, CELL VOLUME AND ORIENTATIONAL ORDER IN FULLERIDE SUPER-CONDUCTORS - THE SEARCH FOR EXPANDED Pa3 SYMMETRY PHASES. P. Durand, M.J. Rosseinsky, Univ of Liverpool, Dept of Chemistry, Liverpool, UNITED KINGDOM; Y. Dubitsky, A. Zaopo, Pirelli Cavi e Sistemi, Milan, ITALY.

The transition temperatures of the A_3C_{60} superconductors increase with interfulleride separation. The rate of increase depends strongly on the mode of interfulleride overlap, with a much more pronounced dependence in the Pa3 symmetry Na_2AC_{60} phases than in those with the Fm3m structure of K_3C_{60} . The highest T_c in the Pa3 family is found for Na_2CsC_{60} (12K). The demonstration of higher T_c 's in this family requires the preparation of examples with larger lattice parameters, and we have therefore investigated the substitution of potassium for sodium on the tetrahedral sites. We will present structural, spectroscopic and magnetic characterisation of these expanded $Na_{2-x}K_xCsC_{60}$ phases ($0.1 \leq x \leq 1$). The potassium substitution produces the desired increase in lattice parameter, but suppresses T_c to below the values expected by extrapolation from the pure sodium Pa3 phases.

11:15 AM W1.8

STUDIES OF ENDO-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 CSC/NAS, Moffett Field, CA; Kyeongjae Cho, Stanford University, Dept of Mechanical Engineering, Stanford, CA.

Quantum computers potentially can exceed the computational efficiency of present day classical computers for certain class 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 appreciably with increasing number of qubits and the approach is not scalable to more than 10 qubit systems. As an alternative "solid-state" approaches are proposed in which arrays of suitable atomic dopants, with 1/2 nuclear spin, are required which are questionable from fabrication and stability point of view. [2] Recently, we have proposed the concept of encapsulated, nuclear spin 1/2, dopants for the fabricating appropriate arrays of nuclear spin 1/2 particles in solid-state materials.[3] As examples, a variety of endo-fullerenes encapsulating 1H and ^{31}P as atomic dopants have been investigated using ab-initio total energy pseudo-potential DFT based method. Total energy minimization of 1H and ^{31}P in $C_{20}H_{20}$, C_{36} , C_{60} and compressed bucky onion reveal that in some cases dopants are stable at the center and in some cases on the C atom of the encapsulating wall. The diffusion barriers for the encapsulation and escape have been calculated to estimate the life times, and will be discussed for the suitability in a solid-state quantum computer application.

1. Chung, I.L. et al. *Nature* **393**, 143 (1998).
2. Kane, B.E. *Nature* **393**, 133 (1998).
3. D. Srivastava and K. Cho, DDF Award Proposal at NASA Ames Research Center, Spring 1999.

11:30 AM W1.9

THE INTERACTION OF C_{60} WITH AMORPHOUS SILICON: TWO AND THREE DIMENSIONAL STRUCTURES. P. Reinke, P. Oelhafen, Universität Basel, 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 molecules enclosed by the silicon matrix remain intact thus retaining their characteristic valence band structure. The composite material remains unchanged up to a temperature of around 700°C. UPS spectra recorded at intervals of 20°C during the annealing procedure show that carbide formation begins only at temperatures exceeding 700°C, when the fullerene cages break up and the a-Si matrix undergoes a phase transition to crystalline silicon. The hollow cages formerly defined by the C_{60} might be preserved and now surrounded by thin SiC layers. The charge transfer and electronic 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 dielectric a-Si matrix will be discussed in view of the photoemission 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.

11:45 AM W1.10

IN SEARCH OF THE MOLECULAR TRIPLET IN C_{60} USING LOW TEMPERATURE RAMAN MICROSCOPY. Gordon Chambers, Alan B. Dalton, Hugh J. Byrne, Facility for Optical Characterisation and Spectroscopy(FOCAS), School of Physics, Dublin Institute of Technology, IRELAND.

The Raman scattering signal of C_{60} thin films were monitored as a function of the excitation intensity at 514 nm in the temperature range 77-300K. At temperatures above the well documented phase transition at 249K, the ground state Raman mode, at 1469 cm^{-1} was seen to degrade quickly under illumination to a lower wavenumber of 1458 cm^{-1} , the position of which has been attributed to the solid state C_{60} photopolymer, formed by 2+2 cycloaddition across pi-bonds of neighbouring molecules. During the photopolymerisation process several polymeric and excited state species can be identified in the Raman spectrum. Raman spectroscopy has proven to be an excellent probe of the active species in the photophysics and photochemistry of C_{60} in solution and in the solid state. Indeed when the Raman scattering signal of C_{60} in chlorobenzene solution was monitored at low intensities, the A_{2g} pentagonal pinch mode was positioned at 1469 cm^{-1} and at intensities where an inverse saturable absorption is observable, it was positioned at 1466 cm^{-1} . This mode positioning has been previously ascribed to the molecular triplet state of C_{60} . However, a corresponding Raman signature for solid C_{60} has never been reported. Solid C_{60} satisfies the general topochemical and photophysical requirements for a 2+2 cycloaddition reaction above 249K more readily than in solution. Below this temperature, the solid state undergoes a first order transition from a face centred cubic to a simple cubic orientation. In the low temperature phase, solid C_{60} no longer satisfies requirements for a 2+2 cycloaddition. As a result, at intensities where an inverse saturable absorption for the solid state is observed a reversible shift in the ground state A_{2g} pentagonal pinch mode from 1468 to 1463 cm^{-1} was observed. The mode positioning has been associated with a high intensity excited state previously reported in the solid state C_{60} . Further to this, an intermediate mode positioning of 1466 cm^{-1} was observed similar to the Raman signature of the molecular triplet reported for solution.

SESSION W2: NANOTUBE SYNTHESIS I

Chairs: Patrick Bernier and David E. Luzzio
Tuesday Afternoon, April 17, 2001
Metropolitan I (Argent)

1:30 PM *W2.1

IN-SITU OBSERVATION OF FULLERENE AND NANOTUBE GROWTH PROCESS. Yohji Achiba, Tokyo Metropolitan Univ, Dept of Chemistry, Tokyo, JAPAN.

In order to understand the growth processes of fullerenes and carbon nanotubes, spontaneous emission as well as scattering properties of carbon vapor has been studied in detail, particularly placing special attention to their temperature dependent behaviors. Time, spatial and temperature histories of the laser induced carbon plume gave important information on the fact how the growth of fullerenes and nanotube proceed.

2:00 PM *W2.2

IN SITU INVESTIGATIONS OF SINGLE WALL CARBON NANOTUBE SYNTHESIS BY LASER VAPORIZATION. A.A. Puzos, Department of MS&E, University of Tennessee, Knoxville, TN; H. Schittenhelm, X. Fan, M.A. Guillorn, D.W. Austin, P.F. Britt, S.S. Bromley, S.J. Pennycook, M.L. Simpson and D.B. Geohegan, Oak Ridge National Laboratory, Oak Ridge, TN.

The laser vaporization of carbon targets which contain metal catalysts is one of the most versatile techniques for the synthesis of single wall carbon nanotubes (SWNT) for electronic and structural applications. However electronic transport through SWNT depends sensitively upon their helicity, length, diameter, defect density, and post-synthesis purification treatments, all of which depend upon the processing conditions. Unfortunately, there is very little agreement on the mechanisms or rates for SWNT growth, which are key elements for the production of SWNT with controlled properties or approaches to scale their production. In our study several different time-resolved spectroscopic techniques are applied in situ to form a comprehensive picture of the SWNT growth process by laser vaporization, including intensified CCD-array imaging of Rayleigh scattered laser light and laser-induced luminescence, plasma and laser-induced emission spectroscopy, absorption spectroscopy, and pyrometry. The imaging diagnostics are applied, along with ex situ TEM and FESEM analysis of collected deposits, to estimate the SWNT growth rate by limiting the growth time at elevated temperature. Three different cases of laser vaporization (LV) were investigated: 1) short-pulse LV at 1000°C (8 ns, 1.06 μm); 2) long-pulse LV at 1000°C (a train of ~80,

200ns-pulses, total length 200 μ s, 1.06 μ m); and 3) cw-CO₂-LV at room temperature (10.6 μ m). Raw material collected from different locations in the chamber (indicated by the in situ diagnostics) was characterized by Raman spectroscopy, TEM, and FESEM, and thermogravimetric analysis (before and following 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 sponsored by the U.S. Department of Energy and the Laboratory-Directed Research and Development Program at ORNL under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

2:30 PM W2.3

PERFECTLY ALIGNED SINGLE WALL CARBON NANOTUBE CRYSTALS. Jin Won Seo^{1,2}, James K. Gimzewski², Reto R. Schlittler². ¹Institut de Physique, Université de Neuchâtel, Neuchâtel, SWITZERLAND. ²IBM Research Division, Zurich Research Laboratory, Rüschlikon, SWITZERLAND; 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 (MWCNT's and SWCNT's 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. SWCNT's 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 crystals made of well-ordered SWCNT bundles are directly fabricated using a nano-patterned solid-state reaction in vacuum. Transmission electron microscopy (TEM), Atomic Force Microscopy and Electron Energy Loss Spectroscopy were used to elucidate the structure and unique ordering of the tubes. Single walled tubes within a single crystal were found to be completely straight and have uniform diameters of approx.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 crystallites. Video sequences of aspects of the growth process using in-situ heating in the TEM will also be used to illustrate the basic growth mechanism. [1] Iijima, Nature 354 (1991) 56. [2] A. Thess et al., Science 273 (1996) 483. [3] Y. Zhang et al., Science 285 (1999) 1719.

2:45 PM W2.4

THE TUBE-TUBE INTERACTIONS, GAS EXPOSURE AND ALKALI-METAL INTERCALATION IN SWNT BUNDLES STUDIED BY NUCLEAR MAGNETIC RESONANCE. Xiaoping Tang, Hideo Shimoda, Alfred Kleinhammes, Les Fleming, Bo Gao, Otto Zhou, 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 quantitative values of the electronic density-of-states 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.

3:30 PM *W2.5

CARBON AND BORON-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 PM W2.6

NUCLEATION AND GROWTH OF CARBON CONES FROM MONOCYCLIC CARBON RINGS. M.M.J. Treacy and J. Kilian, 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 expectations, there are five distinct cone angles possible, corresponding to the

number of disclinations, m , supported by a graphite sheet. In addition, flat graphitic disks are observed as well as wide hollow tubes. Transmission electron microscopy revealed that the most 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 it is a natural consequence of graphite growth that has been seeded by monocyclic carbon rings, C_n . For large rings with $n > 10$, we show that most growth modes will result in $m = 3, 4$ cones.

4:15 PM W2.7

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

Mono-sized and single-walled carbon nanotube (SWNT) arrays, synthesized by pyrolyzing tripropylamine molecules in the channels of porous zeolite single crystals (AFI), have been evidenced by high-resolution transmission electron microscopy (HRTEM). The AFI used is a type of microporous crystal. The one-dimensional channels in the crystals packed in hexagonal array, have an inner diameter of 0.73 nm. During the initial growth of AFI, tripropylamine was introduced into the channels. The subsequent thermal treatment of AFI crystals at 500-800°C in vacuum led to the pyrolysis of carbon and the formation of SWNTs in the AFI channels. The resulting AFI crystallites show good polarization characteristics. While normal AFI crystals are transparent and isotropic in character. SWNTs were extracted by dissolving the AFI framework in HCl acid. The SWNT-containing solution was subsequently enriched and dispersed on carbon lacey 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 ultra-small-SWNTs were imaged as paired fringes. The spacing and shape of the paired fringes are sensitive to the focus condition of HRTEM. When imaging is done at Scherzer defocus condition, the spacings between the paired dark fringes (outside-to-outside) represent the actual diameters of the SWNTs.

4:30 PM W2.8

SPONTANEOUS FORMATION AND STABILITY OF GaP CAGE STRUCTURES: A THEORETICAL PREDICTION OF A NEW FULLERENE. F. Buda, Department of Theoretical Chemistry, Vrije Universiteit, Amsterdam, THE NETHERLANDS; V. Tozzini, INFN and Scuola Normale Superiore, Pisa, ITALY; A. Fasolino, 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 possess a graphite-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 suggests the stability of hetero-fullerenes formed by a compound with zincblend bulk structure. Our prediction is supported by several indicators: these clusters show closed electronic shells and relatively large energy gaps; the ratio between the cohesive energy per atom in the cluster and in the bulk is very close to the value found for boron-nitride and carbon fullerenes of the same size; the clusters are thermally stable up to a temperature range of 1500-2000 K and they do not dissociate and remain in the same structure when ionized. This work might stimulate experimental groups to widen their search for hetero-fullerenes also to III-V semiconductor compounds.

4:45 PM W2.9

SWNT NUCLEATION: ENERGETICS OF ZIPPING-EDGE MECHANISM. Slava V. Rotkin, Beckman Institute, UIUC, Urbana, IL; Ioffe Institute, St. Petersburg, RUSSIA.

It is intriguing that, despite of the years of experimental study and theoretical modelling, formation of SWNTs is not explained. SWNT nucleation is one of important questions to the theory because the growth might not change nucleus helicity or radius. It follows to 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 very rare event basing 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 scrolling into complete sphere which is the dead 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 directed structure. The generatrix for the formation process is given by the edge of graphite layers. The most stable is the zigzag [1000] edge of graphite. Hence, the most probable is the formation of [0110] (armchair) 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 zipping shows that the optimal diameter of cylindrical nucleus is about 15 Å depending on the ratio of elastic energy to van-der-Waals interaction. The nucleus length depends only on the quality of the initial graphene material owing to the zipping happens when the nucleating cylinder meets sp^3 lattice defect interconnecting two adjacent layers of graphite. Summarising, our novel mechanism explains the prevalent formation of armchair nucleus with diameter 15 Å which is fairly close to experimentally found [10,10] SWNTs.

SESSION W3: NANOTUBE SYNTHESIS II
Chairs: David B. Geohegan and Andrew G. Rinzler
Wednesday Morning, April 18, 2001
Metropolitan I (Argent)

8:30 AM W3.1

SYNTHESIS OF VERTICALLY ALIGNED CARBON NANOFIBER FILMS BY RF MAGNETRON SPUTTERING. Kuei-Yi Lee, Keiichi Fujimoto, Shigeharu Ohkura, Shin-ichi Honda, Mitsuhiro Katayama, Kenjiro Oura, 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 considerably depends on the alignment of the carbon nanofibers. For the application, aligned carbon nanofibers have been a candidate 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^{-2} Torr. Silicon wafers were used as substrates. Before attaching the substrates to the chamber, Ni films were deposited on the Si substrates by electron beam evaporation system and then the Ni/Si substrates were treated by HF dilution to make the Ni 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 10^9 to 10^{10} 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 Komiya, Shigekazu Ohmori, Akifumi Yao, Fujio Okino, Hidekazu Touhara, Department of Chemistry, Faculty of Textile Science & Technology, Shinshu University, Nagano, 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 electron field emission sources and nano-electric components. Although there are many methods to prepare the nanotubes such as laser-ablation and arc-discharge, one of 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 7-30 nm in diameter were synthesized in the presence of cetyltrimethylammonium bromide (CTAB, Aldrich) surfactant and triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-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, N_2 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. N_2 was used as a carrier gas. The mesoporous silica with carbon deposit was washed with an excess amount of HF solution at room temperature to dissolve silica. 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 Bernier, Ingrid Stepanek, Robert Almairac, Vincent Jourdain, GDPC, Univ of Montpellier II, FRANCE; Brigitte Vigolo, Alain Pénicaud, Philippe Poulin, CRPP, CNRS, Pessac, FRANCE; Marion Becher, Michael Hirscher, 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 sample quality, (ii) various processing techniques to transform the initial mat of micron long nanotubes into a usable material. While the HiPCO (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 anisotropic materials. We will describe the process to obtain such systems and their characteristics.

9:30 AM *W3.4

CHEMICAL ROUTES TO NANOTUBE 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. The general growth approach involves chemical vapor deposition on catalytically patterned substrates. In the second part, I will show that controlled growth allows for integration of nanowires into measurable 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 intra-tube pn junctions showing rectifying and Esaki diode behavior will be presented.

10:30 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. Grown in long ropes they are expected to form the strongest fiber ever made, with a tensile strength approximately 100 times stronger than steel at only one-sixth the weight. Short lengths derivitized at the ends will constitute a new branch of organic chemistry. These Buckytubes may bring into reality old dreams of molecular electronics, and have application in virtually all technologies where electrons flow. Assembled in closest-packed crystalline arrays these tubes will serve as "seed crystals" for the direct, continuous growth of super-strong, light weight membranes, plates, tubes, and other structures made 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 NANOTUBE AND NANOFIBER BASED DEVICES.

Michael Simpson, David Geohegan, Michael Guillorn, Douglas Lowndes, Alex Puzetzy, Derek Austin, Vladimir Merkulov, Shane Bromley, Darren Ellis, Larry Baylor, Phil Britt.

The device research community has become extremely interested in carbon materials (e.g. diamond, hot filament CVD carbon, multi-wall and single carbon nanotubes, and carbon nanofibers) 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 pivotal roles in the practical development of nanoelectronic and nanosensing devices.

However, the mere existence of these properties is not enough to ensure that practical nanoscale devices will follow directly from the significant materials science and mesoscopic physics research. Of particular concern 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 devices. 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 component) are grand challenges facing molecular-scale electronics. 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 catalyst particles and the duration of the growth time control the position, the diameter, and the length of these fibers. Therefore, VACNFs are beginning to find applications in field emission devices (e.g. flat panel displays and vacuum microelectronics), sensors, and actuators. This talk will focus on the obstacles along the road to 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, actuating, and signal processing applications, but to realize their promise it is essential that mutually compatible methods be developed (i) to fabricate the nanoscale electrode 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 liftoff, RIE), to produce gated electrode 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 future research needs outlined.

[1] V.I. Merkulov et al., Appl. Phys. Lett. 76 (24), 3555 (2000).
 [2] M.A. Guillorn et al., submitted for publication in J. Vac. Sci. and Technol. B.
 This work was carried out in part at the Cornell Nanofabrication Facility, supported by NSF under grant no. ECS-9731293, and at Oak Ridge National Laboratory (ORNL), with support from DARPA/MTO under contract no. 1868HH26X1 and from the ORNL LDRD program. ORNL is managed by UT-Battelle, LLC, for the U. S. Dept. of Energy under contract no. DE-AC05-00OR22725.

11:45 AM W3.8
CONTROLLING STEPS DURING EARLY STAGES TOWARD ALIGNED GROWTH OF 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 during the very 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 nucleation 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 under hydrogen plasma. 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 microscopic observations.

SESSION W4: NANOTUBE PROPERTIES AND MECHANICAL APPLICATIONS

Chair: Oleg R. Lourie
 Wednesday Afternoon, April 18, 2001
 Metropolitan I (Argent)

1:30 PM *W4.1
MECHANICS OF CARBON NANOTUBES. Oleg Lourie, Henry Rohrs, Washington University, Dept of Physics, St. Louis, MO; Hui Huang, BioArray Solutions, Piscataway, NJ; Kevin Ausman, Center for Nanoscale Science and Technology, Dept of Chemistry, Rice University, Houston, TX; Richard Piner, Dept of Mech Engineering, Northwestern University, Evanston, IL; Min-Feng Yu, Zyvex, Richardson, TX; Patrick Gibbons, Washington University, Dept of Physics, St. Louis; Rod Ruoff, Dept of Mech Engineering, Northwestern University, Evanston, IL.

A new testing stage that operates inside of a transmission electron microscope is being used to study nanotube mechanics. The focus of this talk will be on tensile loading experiments on single walled carbon nanotubes (SWCNTs), with particular emphasis on the measurement of the force at break of individual SWCNTs. In addition, other results will be briefly presented, such as measurement of stick-slip mechanics and adhesive properties of SWCNTs, and results on cycling deformation of SWCNTs nanoropes.

2:00 PM W4.2
NANOTRIBOLOGY BY AFM ON MULTIWALL CARBON NANOTUBES. Sébastien Decossas, Fabio Comin, ESRF, Grenoble, FRANCE; Lionel Patrone, SCM/DRECAM/CEA, Gif-sur-Yvette, FRANCE; Anne Marie Bonnot, Joël Chevrier, LEPES/CNRS, Grenoble FRANCE.

Carbon nanotube carpets are produced by Hot Filament Chemical Vapor Deposition. Scanning Electron Microscopy and Atomic Force Microscopy (AFM) images reveal that they are composed of hundreds of nanometers to several micrometers long entangled nanotubes. Transmission Electron Microscopy shows that the nanotubes are multiwall with a typical diameter of 15 nanometers. Force curve measurements performed by AFM on these carpets show that the AFM tip interacts with one or several nanotubes, depending on the normal force applied. The interaction of the tip with several nanotubes gives rise to a multi jump behavior. Each jump appears when one or several nanotubes unhook from the tip. The force involved in a jump is the sum of the nanotube-tip adhesion forces. A non-linear regime shows that the nanotubes are elongated when the tip exerts a pulling force on them. Numerical simulations of the mechanical analysis of a simple tip nanotube carpet model reproduce all the experimental features. When performing force curves, the tip catches nanotubes on the carpet. We show that we can then depose the nanotubes on a clean surface with an absolute precision better than 200nm. We can also change the tip and find again the deposited nanotubes. That allows one to use all the AFM modes and to work with a clean tip. Nanotribological experiments performed with air condition AFM on individual deposited nanotubes show that the friction and the adhesion on nanotubes are lower than on Silicon. We also probed the interaction of nanotubes with Ge dots grown by Molecular Beam Epitaxy on an oxidized silicon wafer. We show that Ge dots act as pinning centers for nanotubes and that a continuous displacement of a nanotube over a Ge dot is impossible. Adhesion pilots the pinning center phenomena and elastic deformation the blocking of nanotube by Ge dots.

2:15 PM W4.3
MOLECULAR DEVICE ENGINEERING-FABRICATION OF A NANO-ELECTROMECHANICAL SYSTEM. Ian J. Gelfand, John E. Fischer, Dept of MS&E, Univ of Pennsylvania, Philadelphia, PA; James Hone, Dept of Physics, California Institute of Technology, Pasadena, CA; A.T. Johnson, Dept of Physics, Univ of Pennsylvania, Philadelphia, PA.

The control of matter on the nanometer scale is imperative for future technological applications. Carbon nanotubes, with their nanometer widths and micron lengths, are ideal starting points for constructing nanoscale electromechanical systems (NEMS). We present such a device based on a single suspended multi-walled nanotube. Electrostatic deflectors are patterned around the tube, which is held onto the substrate by another electrode. When a voltage is applied between the tube and the deflection electrode, the tube bends like a rigid beam. This device may have applications in high frequency switching and sensitive electrometry.

2:30 PM W4.4

WEAR CHARACTERISTICS OF ETCHED SILICON AND CARBON NANOTUBE AFM PROBES. T. Larsen, K. Moloni, 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 tapping mode AFM probes to resolve high-aspect-ratio features is limited by the tip half angle on the leading side. For 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 lithographically 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 conducted on a CVD-polysilicon 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 than 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, SBIR Program.

2:45 PM W4.5

PHYSICAL INTERACTIONS OF CARBON NANOTUBES AND CONJUGATED POLYMERS. Alan B. Dalton, Hugh J. Byrne, Dublin Institute of Technology, Facility for Optical Characterisation and Spectroscopy (FOCAS), Dublin, IRELAND; Jonathan N. Coleman, Brendan McCarthy, Marc in het Panhuis, Werner J. Blau, University of Dublin, Materials Ireland Research Centre, Dept of Physics, Dublin, IRELAND; Pulickel M. Ajayan, Rensselaer Polytechnic Institute, Dept MS&E, 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, electron microscopy and Raman scattering. The relative strength of the interaction was seen to depend mainly on backbone conformation and the presence (absence) of solubilising side-groups. In particular, solutions of the co-polymer, poly(m-phenylenevinylene-co-2,5-dioctyloxy-phenylenevinylene) is 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-substituted PPV and carbon nanotubes were also studied. Absorption, emission and Raman spectroscopy indicate a strong electronic interaction with the polymer. The polymer is seen to tune resonant Raman cross-sections for specific tubes. Through local shifts in the Fermi level resonant 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 PM *W4.6

POLARIZATION EFFECTS IN ORIENTED SINGLE WALL CARBON NANOTUBES AND THE STATE OF PROGRESS IN NANOTUBE ACTUATORS. H.H. Gommans, J.W. Alldredge, J. Hwang, H. Tashiro, D.B. Tanner, and A.G. Rinzler, Department of Physics, University of Florida, Gainesville, FL.

Two developments from our recent work having potential technological significance will be presented. The first of these involves 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 polarization dependence of the resonant absorption (which is responsible for the large resonant Raman signal from SWNT). This permits a straightforward analysis of angle dependent polarized Raman data for quantifying the degree of alignment in oriented samples.¹ I 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 described in 1999².

¹J. Hwang, H.H. Gommans, A. Ugawa, H. Tashiro, R. Haggenmueller, K.I. Winey, J.E. Fischer, D.B. Tanner and A.G. Rinzler, "Polarized spectroscopy of aligned single-wall carbon nanotubes", Physical Review B (Rapid)62 (in press,2000).

²R.H. Baughman, C.X. Cui, A.A. Zakhidov, Z. Iqbal, J.N. Barisci, G.M. Spinks, G.G. Wallace, A. Mazzoldi, D. DeRossi, A.G. Rinzler,

O. Jaschinski, S. Roth, and M. Kertesz, "Carbon Nanotube Actuators", Science 284, 1340 (1999).

4:00 PM W4.7

CHEMICAL ADSORPTION OF POLYMER ON CARBON NANOTUBE. Chengyu Wei, Kyeongjae Cho, Department of Mechanical Engineering, Stanford University, CA; Deepak Srivastava, NASA Arnes Research Center, Moffett Field, CA.

Recently carbon nanotubes are considered as nanoscale fibers which can strengthen polymer composite materials. Nanotube-polymer composite materials can be used for micron scale devices with designed mechanical properties and smart polymer coating to protect materials under extreme physical conditions such as microsattelites. 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 PM W4.8

AB INITIO CALCULATIONS OF THE SWNT/METAL INTERFACE. Shu Peng and Kyeongjae 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 obtaining a variety of nanowire 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. 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 deposit on SWNT and surface coverage have been estimated from surface theory of wetting. The difference in bonding character of Al with SWNT(8,0) and Ti with SWNT(8,0) was discussed.

4:30 PM W4.9

ATOMISTIC 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 Fujiwara, Honda R&D Co., Ltd., Wako Research Center, JAPAN.

Using Brenner type Reactive Empirical Bond Order (REBO) interatomic potentials, we perform atomistic simulations to calculate the optimized structures, tensile and bending strengths, and thermal conductivities of both straight and twisted single-walled nanotube ropes (bundles). Specific problems 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 PM W4.10

GROWTH OF CARBON NANOTUBES FROM LIQUID PRECURSORS. Wai Lo and Kamel 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 simple carbon-containing molecules (e.g. C₂H₂ and C₂H₄) or carbon plasma created by laser 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 phase precursors. This technique involves the creation of fine aerosols from the liquid, which are then transferred to heated quartz substrates coated with Ni nano-particles. The Ni nano-particles are synthesized by direct decomposition of Ni acetate on quartz in reducing atmospheres at temperature between 250 - 500°C. The results show that multi-walled carbon nanotubes with diameters between 20 - 50

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 addition, since the system developed is non-vacuum based and capable of delivering high volume of fine aerosols 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, 2001
Metropolitan I (Argent)

8:30 AM *W5.1

LITHIUM STORAGE IN SWNTS AND NANOSTRUCTURED Si. B. Gao, H. Shimoda, X.P. Tang, A. Kleinhammes, S. Sinha, L. Fleming, J. Owens, L.E. McNeil, Y. Wu and O. Zhou, U. of North Carolina, Chapel Hill, NC.

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 show that the reversible Li storage capacity of purified SWNTs increased from LiC₆ to LiC₃ after chemically etching. All the SWNTs become metallic upon Li intercalation with the electronic density of state 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 (n-Si). The energy 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

QUANTIZED PHONON SUBBANDS AND THE THERMAL CONDUCTIVITY OF SINGLE WALL CARBON NANOTUBES. A.T. Charlie Johnson, J. Hone, M. Llaguno, N.M. Nemes, University of Pennsylvania, Dept of Physics and Astronomy, Philadelphia, PA; Z. Benes, J.E. Fischer, University of Pennsylvania, Dept of MS&E, Philadelphia, PA.

Single wall carbon nanotubes have elastic properties that are unprecedented for a molecular solid. Through measurements of the specific heat, we 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 nanotubes have an extremely large thermal conductivity. Along with the specific heat measurements, we will present thermal conductivity measurements of aligned, densified nanotube material and discuss possible applications of this nanomaterial to thermal management.

[1]. J. Hone, B. Batlogg, Z. Benes, A.T. Johnson, and J.E. Fischer, Specific Heat of single-wall carbon nanotubes: phonon quantization in a nanoscale material, *Science* 289, 1730 - 1733 (2000).

9:30 AM W5.3

THREE-TERMINAL NANOTUBE DEVICE WITH MULTIPLE FUNCTIONALITY. F. Léonard, 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 larger 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

THE MECHANISM OF HYDROGEN STORAGE ON SINGLE-WALL CARBON NANOTUBES. M.J. Heben^a, A.C. Dillon^a, T. Gennett^b, L. Grigorian^c, J.L. Alleman^a, K.M. Jones^a, P.A. Parilla^a. ^aNational Renewable Energy Laboratory, Golden, CO; ^bDepartment of Chemistry and Center for Materials Science, Rochester Institute of Technology, Rochester, NY; ^cHonda Research and Development Americas Inc., Detroit, MI.

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 obtaining SWNTs in purities as high as 98 wt% [2], and developed methods to activate these materials for hydrogen storage [3]. 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 ~6.5 wt% on a total sample weight basis. Temperature programmed desorption spectroscopy shows two distinct sites for hydrogen adsorption. Approximately 2/5 ths of the total hydrogen is in a low temperature site that can easily be removed at room temperature. The remaining 3/5 ths of the hydrogen is more stable and requires temperatures in excess of 300°C for complete removal. We have performed in situ 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 the hydrogen adsorption and the relationship between electronic and structural factors. The role of the impurity metal alloy will also be discussed.

1. A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, and M.J. Heben, *Nature* 386, 377, 1997.
2. A.C. Dillon, T. Gennett, K.M. Jones, J.L. Alleman, P.A. Parilla and M.J. Heben, *Advanced Mat.* 11, 1354, 1999.
3. A.C. Dillon, T. Gennett, J.L. Alleman, K.M. Jones, P.A. Parilla, and M.J. Heben, *Proceedings of the 2000 U.S. D.O.E. Hydrogen Program Review* (2000).

10:45 AM W5.5

AB INITIO STUDY OF HYDROGEN ADSORPTION IN CARBON NANOTUBES. Henry Scudder, Gang Lu, and Nicholas Kioussis, 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 6x6 armchair nanotube by placing one and two H atom(s) 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 desorption 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 desorption 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. Sholl, Anastasios Skoulidas, Dept. of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA; Sivakumar Challa, Vahan Simonyan and J. Karl 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 isotopic selectivity. We will also discuss the accuracy of approximate theories 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 of quantum sieving in zeolites from the literature. Time permitting, we will also discuss

recent applications of Molecular Dynamics simulations to assess the transport properties of physisorbed hydrogen in carbon nanotubes. [1] Q. Wang, S. Challa, D.S. Sholl, and J.K. Johnson, Phys. Rev. Lett., 82 (1999) 956.

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 by acid oxidation and were intercalated with lithium by electrochemical method. The cut SWNTs show enhanced electrochemical properties compared to purified SWNTs. The reversible lithium storage capacity of the shortened SWNTs (LiC_3) is about twice that of purified SWNTs ($\sim\text{LiC}_6$), while the voltage hysteresis between intercalation and de-intercalation is 1V 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 Liu, H. Yukawa and M. Morinaga, Nagoya University, Dept. of MS&E, 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 an electrochemical 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 reversible 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. Tang, H. Shimoda, A. Kleinhammes, L. Fleming, B. Gao, O. Zhou, Y. Wu, Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC.

The ^{13}C nuclear magnetic resonance (NMR) technique has been successfully used to measure quantitative value of the electronic density-of-state at the Fermi level ($g(E_F)$) of the 'metallic' tubes in single-walled carbon nanotube (SWNT) bundles (X.-P. Tang, Science Vol. 288, 492 (2000)). In the present work, we measured the field independence and linear temperature dependence of the ^{13}C nuclear spin-lattice relaxation rate ($1/T_1$) 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 ^{13}C $1/T_1$ 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 $g(E_F)$ of the SWNTs.

SESSION W6: FIELD EMISSION

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

1:30 PM *W6.1

FROM NANOCRYSTALLINE DIAMOND TO NANOTUBE FIELD ELECTRON EMITTERS. Oliver Groening, Lars-Ola Nilsson, Pierangelo Groening, Louis Schlapbach, University of Fribourg, Physics Dept., Fribourg, SWITZERLAND; Keneth. A. Dean, 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 the 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 will show that field enhancing structures play a predominate 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 anode field emission measurements and the concept of field enhancement distribution functions (FEDF) in order to obtain a meaning full characterization of planar field emitters. We will show how the experimentally measured FEDFs can be used as inputs for simulation of emission site densities. We will discuss the requirements of nanotube thin films with regards to optimal 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 size effects at the tube 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, Sungho 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 nanotube cathodes. All of the nanotube cathodes were found to emit technologically useful current densities of 10 mA/cm^2 at macroscopic electric fields between 1-5 V/micrometer. In addition, nanotubes cathodes were capable of generating stable current densities in excess of 4 A/cm^2 .

2:15 PM W6.3

SCANNED-PROBE FIELD-EMISSION STUDIES OF RANDOM FORESTS AND ORDERED ARRAYS OF VERTICALLY ALIGNED CARBON NANOFIBERS. Vladimir I. Merkulov, Douglas H. Lowndes, Larry R. Baylor, Michael L. Simpson, Oak Ridge National Laboratory, Oak Ridge, TN; Michael A. Guilorn, 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 $\sim 1 \mu\text{m}$. 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 also were studied, and emission from the individual 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, Nalin Rupasinghe, 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 catalyst layer, acetylene 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 ($10 \text{ V}/\mu\text{m}$) were found for dense 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 than 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.I. Milne, 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 both the emission currents and the emission site density. The films have an onset field of 3 V/ μm . The emission site density is viewed on a phosphor anode and it increases rapidly with applied field. The work function of these films has been measured by Kelvin probe and is always about 4.7 eV. It is assumed that the emission occurs from surface regions with a range of field enhancement factors but with a relatively constant work function; in effect at a constant local field. The emission site density is found to increase exponentially with the inverse of the applied field. This is equivalent to the field enhancement factors having an exponential distribution. This is similar to that found for carbon nanotube films. Resistive ballast layers are used to even out the non-uniformity of emission, but at the expense of lower currents.

3:30 PM W6.6

CARBON NANOTUBE FIELD EMISSION DISPLAYS WITH TRIODE STRUCTURES. J.M. Kim, Y.S. Choi, M.J. Yoon, J.E. Jung, The National Creative Research Initiatives Center for Electron Emission Source, Suwon, KOREA; N.S. Lee, N.S. Park, Y.W. Jin, Display Lab., Samsung Advanced Institute of Technology, Suwon, KOREA; J.H. You, C.G. Lee, S.H. Jo, K.S. Choi, E.J. Chi, S.J. Lee, H.S. Han, B.G. Lee, CRD, Samsung SDI, Suwon, KOREA.

Carbon nanotubes have recently demonstrated a great potential to be applied to field emitter materials due to their high aspect ratios, small tip radii of curvature, high chemical stability, and high mechanical strength. Our group fabricated a field emission display (FED) panel with 4.5 and 9 inch diagonals using single-walled carbon nanotubes. These studies were restricted to diode structures. For full gray scales and high brightness of FEDs, however, a triode structure is required. In this study, we present several different types of new triode structure carbon nanotube FEDs (c-FEDs), including undergate, remote-gate, and normal gate triode structures. In the undergate structure, gate electrodes are located underneath cathode electrodes with an in-between insulating layer. The remote-gate panel is composed of a cathode, a separated gate grid and an anode. The cathode and gate plates are separately manufactured and then assembled together with the anode plate for an integration. The normal-gate c-FED has the same structure as that of the micro-tip FED, but a larger gate hole diameter due to the excellent field emission characteristics of carbon nanotubes. For all structures, screen printing, which is characteristic of a low-cost and well-known technology, is exploited to form electron emitters on the cathode using a paste containing carbon nanotubes. A modulation of gate voltages controls electron emission from the emitters. The three different triode structure c-FEDs will be compared in terms of fabrication processes and field emission characteristics will be compared.

3:45 PM W6.7

ELECTRON FIELD EMISSION PROPERTIES OF CARBON NANOTUBES. I.N. Lin, Materials Science Center, National Tsing-Hua University, Hsinchu, TAIWAN; T.F. Kuo, C.C. Chi, Department of Physics, National Tsing-Hua University, Hsinchu, TAIWAN; K.R. Yuc, T.S. Lai, Dept of Physics, Chung-Yuan Christian University, Chung-Li, TAIWAN; Z.Y. Juang, Department of Engineering and System Science, National Tsing-Hua University, Hsinchu, TAIWAN; C.H. Tsaid, M.J. Chiang, Department of MS&E, National Tsing-Hua University, Hsinchu, TAIWAN; K.S. Liue, H.F. Cheng, Dept of Physics, Natl 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 process, a susceptor capable of absorbing microwave and self-generating the heat is used for heating the substrates up to deposition temperature (~ 1200). The reacting gases such as CH_4 can thus be easily dissociated, reacting with catalysts coated on the substrates localizedly. 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 the as-deposited CNTs/Si is around $\text{Fe} = 0.012$ eV and the electron field emission can be turned-on at around $E_0 = 0.8 \sim 1.2$ V/mm. The CNTs synthesized by microwave assisted-CVD process exhibit the highest electron field emission capability, viz. attaining an electron emission current density as large as $\text{Je} = 12,000$ mA/cm² at $E_a = 2.8$ V/mm applied field. It is ascribed to the high CNTs yield and large CNTs density resulted in this process.

4:00 PM W6.8

CARBON NANOTUBE GROWTH PROPERTIES OF GATED FIELD EMITTER ARRAYS AND DIODE FIELD EMITTERS. I.T. Han, N.S. Lee, J.E. Jung, Samsung Adv. Inst. of Tech, Display Lab, Young-In, Kyoung-Ki; J.H. Yoo, Samsung SDI Co., CRC, Suwon, KOREA; H.J. Kim, J.B. Yoo, Sungkyunkwan Univ, Dept of Materials Engineering, Suwon, KOREA; J.M. Kim, Nat'l Creative Initiative Research Center, Suwon, KOREA.

Vertically aligned carbon nanotubes (CNTs) were grown by a DC-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. $1 \mu\text{m}$ thick SiO_2 was deposited to electrically insulate between cathode Cr and gate Cr deposited onto SiO_2 . Holes were made through gate and insulator with a diameter of $4 \mu\text{m}$. Finally catalytic Ni film was deposited into exposed cathode layer. Diode substrate has the same layer structures with that of 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.

4:15 PM W6.9

EFFECTS OF SULFUR CONCENTRATION ON THE ELECTRON FIELD EMISSION PROPERTIES OF NANOCRYSTALLINE CARBON THIN FILMS. S. Gupta, Univ of Puerto Rico, Dept of Physics; B.R. Weiner, B.L. Weiss, Dept of Chemistry, Univ of Puerto Rico and G. Morell, Univ of Puerto Rico, Dept of Physical Sciences, PR.

Results are reported on the electron field emission properties of intrinsic and S- incorporated nanocrystalline carbon (n-C:S) thin films grown on molybdenum substrates by hot-filament CVD technique from methane-hydrogen (CH_4/H_2) and hydrogen sulphide-hydrogen ($\text{H}_2\text{S}/\text{H}_2$) gas pre mixtures respectively. The field emission properties for the S-assisted films are investigated as a function of sulphur concentration. The S-incorporation also causes microstructural changes, as characterized with ex situ techniques such as SEM, AFM and Raman spectroscopy (RS). S-assisted films show smoother surfaces and smaller grains than those grown without it. The electron field emission properties of S-assisted films are compared to the intrinsic material and the threshold field was found to be almost double than the S-assisted film at a particular concentration and temperature (500 ppm and 900°C respectively). These studies are performed in order to 'tailor-the-material' as a viable cold cathode material and understand low-field emission mechanisms from these S-assisted nanocrystalline carbon thin films.

4:30 PM W6.10

THREE-DIMENSIONAL CALCULATION OF FIELD EMISSION FROM CARBON NANOTUBES USING A TRANSFER-MATRIX THEORY. A. Mayer, N. Miskovsky, P. Cutler, Department of Physics, State College, PA.

We present simulations of field emission from carbon nanotubes, using a transfer-matrix methodology. With this technique, all three-dimensional aspects of the potential-energy distributions are taken into account, including the atomic structure of the nanotube. The structures considered are the metallic (5,5) and the semiconducting (10,0) single-wall carbon nanotubes. A capped (5,5) structure is also considered. Besides usual effects associated with the field-emission process, the total-energy distributions of the field-emitted electrons present peaks that are shifted according to the extraction bias. These peaks turn out to be more pronounced for the semiconducting (10,0) than for the metallic (5,5) configuration. Sharp peaks associated with resonant states at the apex of the emitting structures are observed with the capped (5,5) structure. The model has been refined by considering a multipole expansion of the atomic charges constituting the carbon nanotubes. Using the same formalism with the modified potential, the results obtained exhibit more highly pronounced structures in the energy distributions. The origin of these results will be discussed.

References:

1. A. Mayer and J.-P. Vigneron, Transfer matrices combined with Green functions for the multiple-scattering simulation of electronic projection imaging, Phys. Rev. B 60 (4) 2875-82 (1999).
2. A. Mayer and J.-P. Vigneron, Accuracy-control techniques applied to stable transfer-matrix computations, Phys. Rev. E 59 (4) 4659-66 (1999).
3. A. Mayer, P. Senet and J.-P. Vigneron, Electron scattering by a C60 molecule in a projection configuration, J. Phys. Condens. Mat. 11 (44) 8617-31 (1999).

This work was supported by the Belgian National Fund for Scientific Research and by NSF grant number DMI-0078637 administered by UHV Technologies Inc, Mt. Laurel, NJ.

4:45 PM W6.11

N-DOPED CVD DIAMOND FILMS AS A LOW TEMPERATURE THERMIONIC-FIELD ELECTRON SOURCE. F.A.M. Köck, J.M. Garguilo, B. Brown, R.J. Nemanich, 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 the imaging of electron emission from UV photo excitation and from thermionic-field emission. The samples were imaged in UHV by photo electron emission microscopy (PEEM) using a UV Hg lamp for photoemission excitation. The same instrument was used to obtain the thermionic-field emission electron microscopy images (T-FEEM) 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 15nm resolution. Nitrogen doped diamond films were grown at substrate temperatures from 850°C to 920°C, microwave power of 1300W and 50 Torr chamber pressure using 0.5 vol % methane, 12 vol % nitrogen in hydrogen at a total flow rate of 500sccm. 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 is increased. At ~680°C the T-FEEM 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-FEEM 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 film substrate interface. These results indicate a promising new material for the production of low temperature, high brightness electron sources.

SESSION W7: POSTER SESSION FULLERENES

Chairs: Petra Reinke 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: THERMAL STABILITY AND THE INFLUENCE OF DAMAGE ON THE BEHAVIOR OF C₆₀ ADLAYERS. P. Reinke, P. Oelhafen, Universität Basel, Institut für Physik, Basel, SWITZERLAND; H. Feldermann, II. Physikalisches Institut, Universität Göttingen, GERMANY.

Understanding the interaction of C₆₀ with different surfaces is an important prerequisite for different aspects in the application 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 20°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 BN surface shows a very similar behaviour 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 C₆₀ films which contain a low number of defects (e.g. created by electron irradiation during deposition) the desorption behavior changes dramatically. Only an incomplete desorption 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 cages 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 heterostructures, namely the formation of a Schottky-type barrier.

W7.2

ELECTRICAL TRANSPORT PROPERTIES OF POLY-CRYSTALLINE 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 of the photoconductivity, which are followed by the already previously observed long time persistent 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 can 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 with regard to existing models describing transport in polycrystalline thin film materials.

W7.3

NANO-SIZED [60]FULLERENE-CYCLODEXTRIN STAR MOLECULES. Jeong-Seo Park, Han-Chang Kang, Kurt E. Geckeler, Kwangju Institute of Science and Technology, Dept of MS&E, 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(oxyethylene) 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 star-shaped. The telechelic fullerene derivatives have been prepared via addition reaction of poly(oxyethylene)-based arms with covalently bonded beta-cyclodextrin to [60]fullerene. To this end, a mono-tosylated cyclodextrin derivative has been prepared in pyridine and then reacted with an amino-functional poly(oxyethylene) in the presence of triethylamine. The subsequent reaction of [60]fullerene with the hydrophilic poly(oxyethylene)-conjugated cyclodextrin derivative yielded the star-shaped macrofullerene 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. Bingshe Xu, Xuguang Liu, Xiaoqin Yan, Jinli Qiao^a and Weijun Jin^b, College of Materials Science and Technology, Taiyuan University of Technology, Taiyuan, Shanxi, CHINA. ^aCollege of Science, Taiyuan University of Technology, Taiyuan, Shanxi, CHINA. ^bDepartment of Chemistry, Shanxi University, Taiyuan, Shanxi, CHINA.

The interaction of water-soluble C₆₀ derived fullerols with bovine serum albumin (BSA) in physiological environment was studied in detail by the fluorescence method. Experiments showed that the interaction of fullerols 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 the reaction is 0.63. Besides, the effects of metallic ions such as Cu²⁺, Fe³⁺ and Cr(VI) on the interaction of fullerols 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 interactions between fullerols and BSA, while high concentrations of Fe³⁺ or Cr(VI) favor the interactions between fullerols and BSA.

W7.5

TRANSFORMATION OF ACTIVE CARBON TO ONION-LIKE FULLERENES UNDER ELECTRON BEAM IRRADIATION. Husheng Jia, Bingshe Xu, College of Materials Science and Technology, Taiyuan University of Technology, Taiyuan, Shanxi, CHINA.

The transformation of an active carbon film under Pt nanoparticles to onion-like fullerenes has been in-situ investigated by a high-resolution

transmission electron microscope. It was found that the onion-like fullerenes/metals polycrystalline film was formed under electron irradiation. The formation process was consisted of three steps: first, the flakes of onion-like fullerenes were induced by Pt nanoparticles; second, the flakes grew into a few ellipsoidal graphite shell; and third, a gradual reorganization of the formation of quasi-spheroid graphite shells and the bond of Pt particles was took place. It was a composite film of onion-like fullerenes 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 C₆₀ THIN FILMS ON THE ORDER/DISORDER PHASE TRANSITION. E.A. Katz, D. Faiman, Ben-Gurion Univ of the Negev, J. Blaustein Inst for Desert Research, National Solar Energy Center, Sede Boqer, ISRAEL; A. Isakina, K. Yagotintsev, M. Strzhemechny, Verkin Inst for Low Temperature Physics & Engineering, Kharkov, UKRAINE.

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 impurity content of C₆₀ 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 diffraction 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. Puzosky
Thursday Evening, April 19, 2001
8:00 PM
Metropolitan Ballroom (Argent)

W8.1

CHARACTERISTICS OF CARBON NANOTUBES SYNTHESIZED BY LASER ABLATION PROCESS. Hsiu-Fung Cheng, Chun-Hong Tsai, Department of Physics, National Taiwan Normal University, Taipei, TAIWAN; Teng-Fan Kuo, Ming-Ray Chiang, I-Nan Lin, Materials Science Center, National Tsing-Hua University, Hsinchu, TAIWAN; Kuan-Run Yu, Tzai-Hsin Lai, Department of Physics, Chung-Yuan Christian University, Chng-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 process, the CNTs were collected at 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 the former process, which requires high environment temperature. By contrast, the CNTs are probably grow from the Ni-clusters coated on substrates in the latter process, which needs substantially lower substrate temperature (~650). Furthermore, synthesis of CNTs at room temperature is made possible in the modified laser ablation process by re-exciting the laser induced plume 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. Phillip F. Britt, David B. Geohegan, Alex A. Puzosky, Henrik Schittenhelm, Shane S. Bromley, Xudong Fan, Michael A. Guillorn, Derek W. Austin, Michael L. Simpson, and Stephen J. Pennycook, Oak Ridge National Laboratory, Oak Ridge TN; Jozsef Devenyi, 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 pure SWNT, the current reality is that additional chemical purification treatments are required to remove residual metal catalyst and amorphous plus graphitic carbon from the SWNT. We are currently interested in the production of SWNT for electronic applications. Since the electronic transport through 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 gentlest conditions to avoid damaging the tubes. In this investigation, the effect of the laser pulse width on the production of SWNT and the associated impurities was 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.[1] 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, 200ns-pulses, total length 200 μs, 1.06 μm) were investigated by Raman spectroscopy, TEM, FESEM, and thermogravimetric analysis. The SWNT were then purified by a combination of chemical and/or thermal oxidative treatments and characterized again 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 was sponsored by the U.S. Department of Energy and the Laboratory-Directed Research and Development Program at ORNL under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.
[1] (a) Dillon, A.C.; Gennett, T.; Jones, K.M.; Alleman, J.L.; Parolla, P.A.; Heben, M.J. *Adv Mater* **1999**, *11*, 1354-1358. (b) Dillon, A.C.; Parolla, P.A.; Alleman, J.L.; Perkins, J.D. Heben, M.J. *Chem. Phys Lett.* **2000**, *316*, 13-18.

W8.3

CARBON NANO-FLAKES GROWN BY MICROWAVE CVD. Yihong Wu, National University of Singapore, Electrical and Computer Engr Dept, SINGAPORE.

Carbon nano-structures can be grown in a variety of forms such as nano- or buckytubes, nested spheroidal 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 multiple wall carbon nanotubes were confirmed first on NiFe-coated Si substrates. The typical length of the nanotubes is about 1 micrometer for a 5 minutes growth. The nanotubes are separated from each other though they tend to form clusters. However, when switching over to sapphire substrates with other parameters and conditions remained unchanged, a totally different type of carbon nano-structure was formed which exhibits flake-like shape with a thickness of about 10-20nm and 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 the flakes have "folded" top tips, while some of them show an open top tip. For those with unfolded top tips, one side of the flakes tends to be covered with a layer of short nanotubes or fibers. Good reproducibility has been obtained on substrates with different thickness of NiFe coatings, ranging from 20 to 100nm. Detailed 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. Fazzio, Antônio J.R. da Silva, Universidade de São Paulo, Instituto de Física, São Paulo, SP, BRAZIL; R.J. Baierle, Centro Universitário Franciscano, Departamento de Ciências Exatas, Santa Maria, RS, BRAZIL; Solange B. Fagan, R. Mota, Universidade Federal de Santa Maria, Departamento de Física, 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 from a theoretical point of view. More recently, however, many devices having chemical compositions beyond that of the pure 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 concentrations. All results are based on ab initio total energy calculations in the framework of the density-functional theory within the local density approximation. The Kohn-Sham equations are solved using a localized basis set and Troulier-Martins pseudopotentials. The Brillouin zone is sampled using a special set of **k** points, and all atoms are relaxed until all components of the forces are smaller than 0.05

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 band structure and density of states of both the metallic (6,6) and semiconductor (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.

W8.5

DENSITY FUNCTIONAL THEORY STUDY OF SINGLE WALL CARBON NANOTUBES. Zhiqiang Wang, Ruth Pachter, W. Wade Adams, Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH; Brahim Akdim, Ohio Supercomputing Center, Columbus, OH; Jean Blaudeau, 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 Young's 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

Chairs: Rodney S. Ruoff and Vladimir I. Merkulov
Thursday Evening, April 19, 2001
8:00 PM

Metropolitan Ballroom (Argent)

W9.1

PREFERENTIAL GROWTH OF CARBON NANOFIBERS USING LITHOGRAPHICALLY PATTERNED CATALYSTS. K.B.K. Teo, M. Chhowalla, G.A.J. Amaratunga, J. Robertson, W.I. Milne, Dept of Engineering, University of Cambridge, UNITED KINGDOM; P. Legagneux, G. Pirio, D. Pribat, Thomson-CSF, FRANCE.

It is well known that carbon nanotubes and nanofibres exhibit exceptional field emitting properties. In order to utilise the full potential of carbon nanotubes/nanofibres, it is necessary to be able to synthesize well aligned nanotubes/fibres at desired locations on a substrate (eg. at emitter/pixel locations for a FED). This paper examines the preferential growth of aligned carbon nanofibres 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 nanofibres. 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 catalysts. Prime Novelty: Patterned growth of nanofibres by PECVD is demonstrated.

W9.2

Abstract Withdrawn.

W9.3

THE ELECTRICAL PROPERTY OF VERTICALLY GROWN CARBON NANOTUBE AND ITS APPLICATION TO THE NANOFUNCTIONAL DEVICES. J.U. Chu, K.S. Jung, E.J. Bae, M.K. Kim, B.M. Kim, In. K. Yoo and W.B. Choi, Microelectronics Lab., Samsung Advanced Institute of Technology, Suwon, KOREA.

A highly ordered alumina hole array which size is decreased down to 10nm was fabricated by an anodic oxidation method. Carbon nanotube was grown vertically with thermal CVD at 700-850°C and analysed 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 electrode which connect one 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.

W9.4

STRUCTURAL CHARACTERIZATION OF GaN NANOWIRES FABRICATED VIA DIRECT REACTION OF Ga VAPOR AND AMMONIA. Randolph Jacobs, L. Salamanca-Riba, Univ of Maryland, Dept of Materials and Nuclear Engr, College Park, MD; Maoqi He, I. Minus, P. Zhou, S. Noor Mohammad, J.B. Halpern, Howard Univ, Matls Sci Research Ctr of Excellence, Washington, DC.

We report structural studies of large-scale wurtzite GaN nanowires fabricated by direct reaction of Ga vapor and NH₃. This recently reported growth technique [1], demonstrates processing of GaN one-dimensional structures as thin as 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 materials as reported by other methods. In this study, transmission electron microscopy (TEM) is used to characterize the nanowires, while x-ray diffraction (XRD) and energy dispersive x-ray spectroscopy (EDS) data provide supporting structural/compositional analysis. Our structural investigation reveals the presence of thin hexagonal platelets, 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 [2 $\bar{1}$ 10] direction or parallel to the hexagonal platelet edges. In addition, a growth mechanism is proposed based on the evidence presented in this study.

[1] Maoqi He, I. Minus, P. Zhou, S.N. Mohammad, Joshua B. Halpern, R.N. Jacobs, W.L. Sarney, R.D. Vispute and L. Salamanca-Riba Appl. Phys. Lett. (in press).

W9.5

LITHIUM INSERTION IN NANOPOROUS CARBON MATERIALS PRODUCED FROM CARBIDES. Irina Kotina, Victor Lebedev, Andrey Ilves, Galina Patsekina, Lubov' Tuhkonen, Petersburg Nuclear Physics Institute, Gatchina, Leningrad district, RUSSIA; Sergey Gordeev, Central Research Institute for Materials, St. Petersburg, RUSSIA; Thommy Ekstrom, Skeleton Technologies Group, Stockholm, SWEDEN; Mariya Yagovkina Mehanobr-Analyt Co, St. Petersburg, RUSSIA.

Lithiated carbonaceous 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, Mo₂C) 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 out 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,a)⁴He 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 pirocarbon content. These profiles could be simulated by erfc function. It gave possibility to determine lithium diffusion coefficient (D_{Li}). We determined D_{Li} in the samples under study at various temperatures. Overall the largest values of D_{Li} were obtained for nporC<Mo₂C> and the smallest-for nporC<SiC> (for example, at temperature 100°C $\sim 2 \cdot 10^{-7}$ cm²/sec and $\sim 10^{-8}$ 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 LiC₆, LiC₁₂, LiC₂₄ and LiC₄₀ were observed. Besides Li₂C₂ and Li₂CO₃ phases were registered 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. Matthias Töwe, Petra Reinke, Peter Oelhafen, Inst für Physik, Univ Basel, Basel, SWITZERLAND.

Lithium-containing carbon materials are studied with respect to various applications, e.g., 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 x-ray and ultraviolet photoelectron spectroscopy (XPS, UPS). Usually less than 10at% 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 ions at 50eV to 5keV. 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 2keV 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 induced 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 P. Sullivan and Richard B. Jackman
Thursday Evening, April 19, 2001
8:00 PM
Metropolitan Ballroom (Argent)

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

W10.2
EFFECT OF BACK CONTACTS ON TETRAHEDRAL AMORPHOUS CARBON FILMS GROWN USING THE CATHODIC ARC PROCESS. B.S. Satyanarayana, H. Takahashi*, T. Narusawa* and A. Hiraki, KUT Academic & Industrial Collaboration Centre, Kochi University of Technology, Kochi, JAPAN. *Electronic and Photonic Systems Engineering Department.

Tetrahedral amorphous carbon (ta-C) has been studied with increasing interest for applications in the area of electronic and field emission devices, besides its wide spread use in tribological applications. The major advantage of the hydrogen free diamond like carbon (DLC) or ta-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^3 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] had reported observing nanoclusters in the case of ta-C films grown on aluminium. While the ta-C films grown under identical conditions on silicon substrates were atomically smooth. Thus further indicating some dependence of the material property on the nature of the substrate or back contact. Hence to test the effect of the back contact, a series of ta-C films were deposited under identical conditions onto substrates having 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 ta-C films grown on different metal back contact. SEM and Raman were used to study the structural properties. The studies indicate that the back contact do influence the properties of the material to some extent. These results are analysed with respect to an earlier report regarding, no significant influence of back contacts on field emission from similar ta-C films[2]. [1]. C. Arena, B. Kleinsorge, J. Robertson, W.I. Milne, and M.E. Welland, J. Appl. Phys. 85, (1999) 1609. [2]. A. Hart, B.S. Satyanarayana, J. Robertson & W.I. Milne, Appl. Phys. Lett. 74, (1999) 594.

W10.3
INCORPORATION OF HYDROGEN AND OXYGEN INTO (t)a-C:H THIN FILMS DEPOSITED USING DECR PLASMA. Fabrice Piazza, Centre National de la Recherche Scientifique (CNRS), Laboratoire PHASE, Strasbourg, FRANCE; Dieter Grambole, Folker Herrmann, Forschungszentrum Rossendorf e.V., Institut für Ionenstrahlphysik und Materialforschung Postfach, Dresden, GERMANY; Gary Relihan, National Microelectronics Research Centre (NMRC), University College, Cork, IRELAND; Marie France Barthe, Pierre Desgardin, Centre National de la Recherche Scientifique (CNRS), Laboratoire CERI, Orleans, FRANCE; André 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)a-C:H thin films at RT on single crystal Si substrates RF biased within the range $25 \leq U \leq 600$ V. Acetylene was used as precursor. The plasma pressure was varied within the range $0.1 \leq P \leq 1.5$ mTorr. The films were analysed using Fourier transform infrared spectroscopy (FTIR). The nuclear reaction $^{15}\text{N} \rightarrow ^{12}\text{C} + ^4\text{He}$ γ 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 ($N_H \sim 30\%$ and $V \sim 100 \text{ \AA}/\text{min}$) within the investigated bias range ($25 \leq U \leq 600$ V). At higher pressures ($P \geq 0.5$ 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. Whatever the pressure the probability of hydrogen incorporation is seen to increase with decreasing growth rate. At $P \sim 0.3$ mTorr the FTIR analysis shows that the integrated intensity of the O-H band ($3250\text{-}4000 \text{ cm}^{-1}$) remains constant within the bias range $0 \leq U \leq 150$ V. The corresponding intensity of the C-H 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 into films deposited with $U=80$ V using positron Doppler broadening spectroscopy. Inspection of the C-H stretching band shows that the nature of hydrogen bonding changes when substrate bias is varied while the integrated intensity of the O-H band drops by almost an order of magnitude for the substrate bias higher than 200 V. This work has been funded in the framework of the European Community Brite-Euram Contract N° BRPR-CT98-0749.

W10.4
DEPOSITION OF DIAMOND-LIKE CARBON FILMS BY ELECTROLYSIS OF ACETYLENE-AMMONIA SOLUTION. Andrei Matveev, Inst of Solid State and Semiconductor Physics, Minsk, BELARUS; Patrice Aublanc, Inst National Polytechnique de Grenoble, LMGP, Grenoble, FRANCE; Ludmila Klimkovich, Andrei Genis, Inst of Solid State and Semiconductor Physics, Minsk, BELARUS; Irina Fomikhina, Tatiana Kuznecova, 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 $\langle 100 \rangle$ Si plates were used as electrodes. A d.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 when Si was used for the anode. The films exhibited different crystallinity and different sp^3/sp^2 ratio dependently 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 ~ 0.203 nm and ~ 0.116 nm which are close to those of graphite $4H$ (ASTM No 25-284). ED from the film synthesized on the Si cathode exhibited rings and diffuse halo. Calculated d (nm) values are 0.207 ± 1 , 0.124 ± 1 , 0.106 ± 1 , 0.080 ± 2 . The best assignment of this ED pattern among all known carbon phases was achieved for a cubic lattice with a cell dimension $a = 0.359 \pm 1$ nm. Raman spectrum of the film synthesized on the Ni cathode demonstrated three broad bands with maximums at 1340, 1442 and 1600 cm^{-1} . This spectrum was attributed to an amorphous 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 $\sim 1130\text{ cm}^{-1}$ and three broad bands: $1150\text{--}1350\text{ cm}^{-1}$, $1400\text{--}1500\text{ cm}^{-1}$ and $1600\text{--}1700\text{ cm}^{-1}$. This spectrum was attributed to diamond-like carbon with some fraction of sp^2 bonded carbon. We propose that synthesis of carbon occurs through dehydrogenation and polycondensation of acetylene caused by atomic hydrogen generated on the cathode from reduction of ammonium ions.

1. A.T. Matveev, D. Golberg, V.P. Novikov, L.L. Klimkovich, Y. Bando, Carbon, October 20, 2000.

W10.5

PREPARATION AND PROPERTIES OF AMORPHOUS CARBON OXYNITRIDES $\text{A-CN}_x\text{O}_y$ FILMS MADE BY A NITROGEN RADICAL SPUTTER METHOD AND BY THE LAYER-BY-LAYER METHOD. Yohko Naruse, Shoji Nitta and Hitoe Habuchi*, Department of Electrical Engineering, Gifu University, Gifu, JAPAN. *Gifu National College of Technology, Gifu, JAPAN.

We have prepared very interesting amorphous carbon nitride a-CN_x films by a nitrogen radical sputter method. With atomic hydrogen treatment of a-CN_x , we have obtained good electronic properties with fewer defects. We have used the cyclic process of the deposition of a-CN_x by a nitrogen radical sputter and of the etching by hydrogen plasma and obtained the layer-by-layer LLa- CN_x with good electronic properties. In this paper, the effect of oxygen plasma on a-CN_x was studied. It is not possible to get a oxidized carbon nitride film by introducing both of nitrogen and oxygen as sputter gases. It is confirmed that the oxygen plasma has three effects on a-CN_x ; One is an etching of a-CN_x decreasing the film thickness. The other is to oxidize a-CN_x and producing amorphous carbon oxynitride $\text{a-CN}_x\text{O}_y$ films. The third one is the termination of pair defect states in a-CN_x and decreases defect density. The occurrence of these three depend on the preparation conditions. $\text{A-CN}_x\text{O}_y$ films show higher optical gaps and smaller defect densities from experiments on XPS, optical transmittance 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-CN_x to more porous $\text{a-CN}_x\text{O}_y$. These two properties are good for applications of $\text{a-CN}_x\text{O}_y$ to luminescent materials and also as a low dielectric constant materials. We have studied the deposition of a-CN_x on $\text{a-CN}_x\text{O}_y$. A-CN_x deposited on $\text{a-CN}_x\text{O}_y$ contains a lot of defects. This was confirmed by making the layer-by-layer amorphous carbon oxynitride LLa- CN_xO_y with a cyclic process of the deposition of ultra thin a-CN_x by a nitrogen radical sputter method and of the oxidation by the oxygen plasma treatment.

W10.6

HARD CARBON FILMS CONTAINING TITANIUM AND BORON CARBIDE. Ayako Kimura, Yasushi Azuma, Kunihiro Yamada, Tetsuya Suzuki, Keio Univ, Dept of Mechanical Engineering, Yokohama, JAPAN.

Ceramics thin films such as TiN, TiC and (Ti,Al)N synthesized by the cathodic arc ion plating 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 difficulties to keep stable arc-discharge during the deposition, 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 macroparticles are emitted from the carbon cathode. As a result, the surface of films is contaminated with these macroparticles and becomes very rough. In order to solve the above problems, we focused on controlling the microstructure and electrical conductivity of the carbon cathodes by the addition of conductive powder during the sintering of carbon. C, Ti and B_4C 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_4C was changed to seek the best condition for electrical conductivity and behavior of arc-discharge. Furthermore, pyroid 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 the cathodic arc ion plating method. In this paper, we report that surface roughness and adhesion strength of hard carbon films could be improved by controlling microstructure of carbon cathodes.

W10.7

PARAMAGNETIC CENTERS IN AMORPHOUS CARBON-BASED THIN FILMS. Malek Tabbal, Theodore Christidis, Samih Isber, Dept of Physics, American University of Beirut, Beirut, LEBANON; My Ali El-Khakani, Philippe Mérel, 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-CN) thin films. DLC and a-SiC films have been deposited on Si by pulsed laser ablation using a KrF excimer laser, while the a-CN films were synthesized using the same system combined with a nitrogen surface wave plasma. For all three types of films, the spin density was found to be of the order of 10^{20} spins/ cm^3 but it varies with deposition conditions such as 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 the films are most probably clustered sp^2 carbon related defects leading to an exchange narrowed EPR room-temperature linewidth ranging from 2.2 to 8 Gauss. The thermal dependence of the EPR linewidth is also investigated and discussed in terms of the conduction mechanisms in the films. In a-SiC, the increase of the EPR linewidth with temperature is attributed to spin hopping between neighboring sp^2 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-CN films, an increase in nitrogen incorporation (17 to 25% atomic) leads to a narrowing of the EPR line. This latter effect could be explained by the occurrence of nitrogen bridging between adjacent paramagnetic centers so that 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 CARBON CLUSTERS IN NANOPOROUS CARBON PRODUCED FROM CARBIDE MATERIALS. A.M. Danishevskii^a, S.K. Gordeev^b, A.V. Grechinskaya^b, T. Ekstrom^c. ^aIoffe Physico-Technical Institute, St. Petersburg, RUSSIA. ^bCentral Science Research Institute for Materials, St. Petersburg, RUSSIA. ^cSkelton 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 900°C was 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 10-20 Å, 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 maxima are shifted from usual values. For example, G band maximum is localized near $1600\text{--}1602\text{ cm}^{-1}$ on frequent occasions. Raman spectra for np-C samples produced from varied carbides are differentiated. Both of wide bands undergo shifts in going from the exciting line 488 nm to 647 nm 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 - 300 cm^{-1} . Their positions do not coincide with Raman lines of water, oxygen or nitrogen which could be adsorbed 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 all 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. Obtained data enable to propose some model of the fragment structure underlying of the carbon skeletons in these materials.

The studies were carried out on NPC samples developed and produced in collaboration with Skelton Technologies Group. This research was fulfilled with the support of RFBR(99-0217984) and Skelton Group, Sweden.

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W10.9

ELECTRICAL CONDUCTIVITY AND ELECTRON SPIN RESONANCE STUDY OF NITROGENATED ULTRA-NANOCRYSTALLINE DIAMOND FILMS. Somnath Bhattacharyya, H. Wang, J. Schlueter, O. Auciello, J.A. Carlisle, D.M. Gruen, Materials Science and Division, Argonne National Laboratory, Argonne, IL.

Ultrananocrystalline diamond (UNCD) thin films were synthesized by microwave chemical vapor deposition using a gas mixture of argon, methane and up to 20% nitrogen in the plasma. Films prepared without adding nitrogen are highly insulating, whereas the conductivity of the UNCD films increases from about 0.001 (Ohm.cm)⁻¹ to 150 (Ohm.cm)⁻¹ for films grown with 1% or 20% nitrogen in the plasma, respectively. TEM results indicate that the grain size and grain boundary width increase with increasing nitrogen incorporation into the films, with the grains consisting of essentially pure diamond whereas the grain boundaries contain significant p-bonding. These findings are in agreement with recent molecular dynamics calculations. The data from temperature dependent conductivity and Hall measurements indicate that, as more nitrogen is incorporated into the films, nearest-neighbor hopping (NNH) conduction becomes dominant over the band conduction that is prevalent at lower concentrations. The finite conductivity exhibited by all the nitrogen-incorporated films at temperatures approaching 10 K is characteristic of a semi-metal. In addition, the Hall and spin resonance measurements show that the nitrogen may be incorporated in the UNCD films as electrically active dopants. Electronic spin resonance (ESR) data indicate that the concentration of spins increases with nitrogen gas percentage in the plasma up to 5%. However, the ESR signal from films grown with 15%-20% N₂ are very weak compared to all other samples. The decrease of ESR signal intensity can be explained by the delocalization of spin centers and/or pairing of the spins of the donors or carriers present in the materials. The spin density and width of the ESR lines depend weakly on the sample temperature and follow the Curie-Weiss law of spin susceptibility. The ESR data are also supported by the NNH model of conduction.

SESSION W11: DIAMOND-LIKE CARBON

Chairs: Thomas A. Friedmann and Andre Golanski
Friday Morning, April 20, 2001
Metropolitan I (Argent)

8:30 AM *W11.1

SYNTHESIS OF ULTRATHIN ta-C FILMS BY TWIST-FILTERED CATHODIC ARC CARBON PLASMAS. André Anders, Lawrence Berkeley National Laboratory, Berkeley, CA; Ashok V. Kulkarni, Read-Rite Corporation, Fremont, CA.

The application of cathodic-arc-deposited films has been very slow due to the infamous macroparticle problem. Many attempts have been made to synthesize superior films by overcoming the macroparticle issue and utilizing the outstanding properties of cathodic arc plasmas. Magnetic plasma filtering was introduced in the late 1970s and major improvements have been made since. Here we report about the application of the most advanced filter to-date: the twist filter as the key component to an open-architecture, pulsed carbon plasma system. Ultrathin (< 5 nm) amorphous carbon (a-C) films have been deposited on 6 inch wafers. Film properties have been investigated with respect to application in the magnetic data storage industry.

9:00 AM *W11.2

TETRAHEDRAL AMORPHOUS CARBON (AMORPHOUS DIAMOND) MECHANICAL DEVICES. J.P. Sullivan, T.A. Friedmann, R. Hohlfelder, M.P. de Boer, M.T. Dugger, W.K. Schubert, C.I.H. Ashby, M. Mitchell and R.G. Dunn, Sandia National Laboratories, Albuquerque, NM; D.A. LaVan, Massachusetts Institute of Technology, Cambridge, MA.

The recent revolution in surface micromachining now enables complete mechanical devices to be synthesized entirely out of thin film materials. This provides a great opportunity to create structural components, i.e. load-bearing or force-transmitting beams, springs, gears, etc., out of materials that formerly found use only as coatings on macroscopic parts. This is particularly true for tetrahedral amorphous carbon (amorphous diamond) films, as these materials possess unique mechanical behavior yet can only be synthesized (in a reasonable time period) as thin films of up to a few microns in thickness. We describe recent developments in the creation of mechanical structures and microelectromechanical systems (MEMS) fabricated from amorphous diamond. These structures include electrostatic comb drive motors, beams, springs, tensile test samples, and friction test structures all with critical dimensions as small as one micron. The unusual atomic structure, bonding, and chemistry of

amorphous diamond makes these mechanical devices particularly interesting. These properties include the existence of a two-phase microstructure, described as interpenetrating nanophases of 4-fold and 3-fold coordinated carbon, which enables plastic-like mechanical deformation of the material. This property allows the residual strain in the films to be reduced below 0.00001 – a critical requirement for the creation of microscopic structures. Other properties include a very high elastic modulus, approaching 800 GPa, and high fracture strength, ~ 8 GPa. The high strength permits ultra-thin free-standing membranes of amorphous diamond to be synthesized (0.1 micron thick), and we describe their use as a vibrating mechanical resonator functioning as a chemical sensor. Lastly, the material is chemically inert and biologically compatible as tested through ex vivo cell-adhesion studies, which should enable future bioMEMS structures. Sandia is a multiprogram laboratory operated by Sandia Corp., a Lockheed Martin Co., for the U.S. Dept. of Energy under contract DE-AC04-94AL85000.

9:30 AM W11.3

NANOSTRUCTURED CARBON FILMS FOR ADVANCED MICROSENSORS. M.P. Siegal, W.G. Yelton, D.L. Overmyer, D.R. Tallant and P.N. Provencio, Sandia National Laboratories, Albuquerque, NM.

Nanostructured carbon consists of highly disordered clusters of graphene-like structures. The degree of bonding disorder and morphological richness are controlled by the energetics of film growth. These films grow at room temperature and have negligible film stress, meaning that that can grow on any substrate to any desired thickness. We have studied forms of nanostructured carbon with various morphologies for absorbent response in surface-acoustic-wave microsensors. Many of the analyte gases tested have response sensitivities greater than an order of magnitude over conventional absorbent materials. Intriguingly, the sensor response is not a function of increasing surface morphology, but rather appears to optimize for carbon films with a particular graphene-bonding character. We will present microstructural and chemical bonding properties from nanostructured carbon films as a 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. LiBassi, 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 films (ta-C) grown with an S-bend filtered cathodic vacuum arc (FCVA), and of hydrogenated ta-C (ta-C:H) grown by a high plasma density source, an electron cyclotron wave resonance (ECWR) reactor. The results indicate that XRR can measure films as thin as 2 nm, which is the range required for carbon overcoats for magnetic hard disks and sliders if they are to reach storage densities of 100 Gbits/in². The density of the films was derived by the critical angle of total external reflection and the best model for other structural parameters (thickness, internal layering and surface roughness) was obtained by fitting a calculated curve to the experimental data. The structure of the films usually consists of a high density layer and of a less dense 0.5-1-nm surface layer and a 0.5-1-nm layer at the film-substrate interface. The structure of the ultrathin S-bend ta-C films resembles that of the thicker S-bend films, with a scaling of the bulk layer thickness, but not of the surface and interface layers (that are ~1 nm in both thick and thin films). A comparison with other techniques for the analysis of thin films is also proposed.

10:30 AM *W11.5

A MODEL TO INTERPRET THE RAMAN SPECTRA OF DISORDERED, AMORPHOUS AND NANOSTRUCTURED CARBONS. Andrea Carlo Ferrari Department of Engineering, University of Cambridge, Cambridge, UNITED KINGDOM.

Raman spectroscopy is a very popular, non-destructive tool for the structural characterisation of carbons. Raman scattering from carbons is always a resonant process, in which those configurations whose band gaps match the excitation energy are preferentially excited. Any mixture of sp³, sp² and sp¹ carbon atoms always has a gap between 0 and 5.5 eV, and this energy range matches that of IR-vis-UV Raman spectrometers. This implies that understanding the resonant Raman process in carbon systems will give a very powerful, fast means for the structural and electronic characterisation of these systems. The Raman spectra of carbons do not follow the vibration density of states, but consist of three basic features, the G and D peaks around

1600 and 1350 cm^{-1} and an extra T peak, for UV excitation, at $\sim 1060 \text{ cm}^{-1}$. The Raman spectra at any wavelength depend on 1) clustering of the sp^2 phase, 2) bond length and bond angle disorder, 3) presence of sp^2 rings or chains, and 4) the sp^2/sp^3 ratio. It will be shown how the basic features of the Raman spectra vary by rationalising them within a three-stage model of order of carbons [1]. This model considers the effects on the Raman of the progressive introduction of disorder in a graphite layer. An amorphisation trajectory is defined, consisting of three stages from graphite to sp^3 amorphous carbon: 1) graphite to nanocrystalline graphite, 2) nanocrystalline graphite to sp^2 amorphous carbon, 3) sp^2 amorphous carbon to sp^3 amorphous carbon. The most common wavelength used for Raman scattering experiments lie in the visible range. It is shown how the three-stage model can account for the vast range of experimental data available in visible Raman experiments. This model can also account for apparently contradictory trends reported in literature, since the clustering of the sp^2 phase and the sp^3 to sp^2 conversion are separately treated. The model will then be extended to explain the dispersion of the Raman peaks when multi-wavelength investigations are conducted [2].

[1] A.C. Ferrari, J. Robertson, Phys. Rev. B 61, 14095 (2000).
 [2] A.C. Ferrari, J. Robertson, Phys. Rev B, submitted (2000).

11:00 AM W11.6

ELASTIC CONSTANTS OF NANOMETER THICK DIAMOND-LIKE CARBON FILMS. Marco G. Beghi, Carlo E. Bottani, Andrea Li Bassi, Rosanna 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 nanometers 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 on softer substrates, still 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 about 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 sp^3 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 4.5 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 has been reported. We thus show that we can grow and characterise 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.

11:15 AM W11.7

NITROGEN DOPING OF TETRAHEDRAL AMORPHOUS CARBON FILMS: SCANNING TUNNELING SPECTROSCOPY. Somnath Bhattacharyya, K. Walzer, M. Hietschold, F. Richter Institut für Physik, TU-Chemnitz, Chemnitz, GERMANY.

Amorphous nitrogenated carbon films with nitrogen atomic concentration between 12 and 30% were deposited using a filtered cathodic vacuum arc and a Kaufman-type ion source. The surface topography of the samples has been investigated by scanning tunneling microscopy (STM) in ultra-high vacuum, showing that the roughness of the film surface decreases with nitrogen concentration. Scanning tunneling spectroscopy (STS) is employed to understand the role of nitrogen in the change of the surface microstructure and electronic structure near the Fermi level. The tunneling current (I) as a function of bias voltage (V) curve is flat at low bias regions indicating a finite gap for the sample with low (12%) nitrogen concentration. An increase of tunneling current and its non-linearity along with the decrease of energy gap occurs in the samples with increase of N concentration. The observed surface density of states $[(dI/dV)/(I/V)]$ has been fitted as a square-root function of bias voltage. An improvement of the quality of these fits in the films with the increase of nitrogen concentration suggests that the defect density of states near the Fermi level (EF) decreases. These analyses could be

attributed to the modification of the structure of amorphous carbon by a large concentration of nitrogen in the films.

11:30 AM W11.8

NITROGEN BONDING STRUCTURE IN AMORPHOUS AND FULLERENE-LIKE CARBON NITRIDE THIN FILMS. N. Heggren, R. Haasch, R. Twesten, Frederick Seitz Materials Research Laboratory and the Materials Science Department, University of Illinois, Urbana, IL; E. Broitman, L. Hultman, Thin Film Physics Division, Department of Physics, Linköping University, SWEDEN; J.E. Greene and I. Petrov, Frederick Seitz Materials Research Laboratory and the Materials Science Department, University of Illinois, Urbana, IL.

The bonding structure of nitrogen in d.c. magnetron sputtered CN_x ($0.1 \leq x \leq 0.7$) films have been studied by in-situ x-ray photoelectron spectroscopy (XPS), and electron energy loss spectroscopy (EELS). Films of various structures (amorphous and fullerene-like) were grown at different conditions, in order to study the effect on the nitrogen bonding structures. The XPS N1s peak showed two distinct peak components at 398.2 eV (P1) and 400.7 eV (P2). In addition, smaller contributions were identified at ~ 399.0 eV (P3) and ~ 402.5 eV (P4). By following the evolution of the different peak intensities during in-situ annealing up to 1000°C in the XPS and EELS systems, a correlation is found between P1 and the EELS pre-peak at ~ 399 eV. This suggests that P1 mainly correspond to N bonded in a pyridine-like environment, i.e., at the edge, or next to a carbon vacancy inside of a graphitic structure. Thus, P1 cannot be explained by N solely bonded to sp^3 C, as is commonly suggested in the literature. When growing films at high pressures, P1 becomes larger, which further support the assignment to pyridine-like N, as these samples were porous and this bonding environment can be more expected. P2 can be assigned to N substituted in a graphitic or fullerene-like structure. For lower growth temperatures, this peak shifts to lower energies due to amorphization and consequent lack of structural order. P3 can most likely be assigned to small amounts of nitrile bonds. Angular resolved XPS measurements show more nitriles and pyridine-like N near the sample surface, while more graphitic N is found in the bulk. The reactivity of the samples when exposed to air and H_2 , as well as the effect of ion sputter cleaning will also be discussed. The latter study shows that high-energy sputter etching can seriously affect the bonding structure in CN_x films.

11:45 AM W11.9

ACOUSTIC MICROSCOPY AND SURFACE BRILLOUIN SCATTERING OF AMORPHOUS CARBON PRESSURE-SYNTHESIZED FROM C_{60} . P.V. Zinin, M.H. Manghnani, S. Tkachev, X. Zhang, School of Ocean and Earth Science and Technology, University of Hawaii, Honolulu, HI; A.G. Lyapin, V.V. Brazhkin, I. A. Trojan, Institute for High Pressure Physics, Russian Academy of Sciences, Troitsk, Moscow, RUSSIA.

The discovery of fullerene molecule C_{60} has led to considerable interest in the elastic properties of fullerenes and fullerene-based materials. Several new stable fullerite phases demonstrate a wide range of properties from fragile crystals to superhard phases. The existence of ultrahard fullerene phase with hardness higher than diamond was recently discussed, though such phases can be obtained only in extremely small size. Here, we report the first successful measurements by Brillouin scattering (BS) and scanning acoustic microscopy (SAM) of the elastic properties of small specimens of amorphous carbon obtained from C_{60} under high pressure and temperature. The superhard phases of amorphous carbon were synthesized from C_{60} at pressure 13 - 13.5 GPa and temperature 800-900°C. Two types of surface waves have been detected by BS in superhard samples: surface Rayleigh wave and lateral longitudinal wave. Velocity of the Rayleigh surface wave measured by BS was in agreement with that measured by acoustic microscope. Simultaneous measurements of the Rayleigh and lateral longitudinal wave velocities make it possible to determine shear and bulk elastic moduli of the specimens. Obtained elastic properties for amorphous carbon synthesized under pressure 13.5 GPa and temperature 900°C are close to those for diamond, indicating that bonds among amorphous carbon network are diamond bonding dominated. The results of these measurements are of importance in understanding the problem of phase transition of C_{60} under high pressure and temperature and particularly the issue of existing ultra and superhard phases.

SESSION W12: DIAMOND AND DIAMOND-LIKE CARBON

Chairs: Michael P. Siegal and John Robertson
 Friday Afternoon, April 20, 2001
 Metropolitan I (Argent)

1:30 PM W12.1

MEDIUM-RANGE ORDER STRUCTURES OF AMORPHOUS

DIAMOND-LIKE CARBON FILMS. Xidong Chen, J. Murray Gibson, Materials Science Division, Argonne National Laboratory, Argonne, IL; John Sullivan and Tom Friedmann, Sandia National Laboratory, Albuquerque, NM.

Hydrogen-free amorphous diamond-like carbon films have stimulated great interest because of their useful properties, such as high hardness, chemical inertness, thermal stability, wide optical gap, and negative electron affinity. These films often contain significant amount of four-fold bonded carbon, to the contrary of amorphous carbon films prepared by evaporation or sputtering, which consist mostly of three-fold bonded carbon. The structure configurations of these three-fold and four-fold carbon atoms certainly decide the properties of these amorphous diamond-like carbon films. We have studied medium-range order structures in these amorphous diamond-like films with fluctuation microscopy. By analyzing speckle dark-field images taken over different areas as a function of momentum transfer in reciprocal space, we measured the pair-pair alignment correlation function for both thermally annealed samples and unannealed samples. We have found that thermal annealing introduces medium-range order in amorphous diamond-like carbon films, causing more pairs of atoms to be aligned. These results agree with density-functional simulations. Larger-scale simulations will be needed to fully understand our experimental results.

1:45 PM W12.2

NANO-STRUCTURED AMORPHOUS CARBON FILMS SYNTHESIZED USING DECR PLASMA. André Golanski, Philippe Kern, Fabrice Piazza, Jean-Paul Stoquert, Centre National de la Recherche Scientifique (CNRS), Dept. PHASE, Strasbourg, FRANCE; Jean Hommet, Centre National de la Recherche Scientifique (CNRS), Dept. IPCMS, Strasbourg, FRANCE; Liam McDonnell, Centre for Surface and Interface Analysis, Dept. of Applied Physics and Instrumentation, Cork Institute of Technology, Cork, IRELAND; Dieter Grambole, Folker Herrmann, Forschungszentrum Rossendorf e.V., Institut für Ionenstrahlphysik und Materialforschung, Dresden, GERMANY.

Diamond-like amorphous carbon (DLC) thin 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 power operating at a frequency of 2.45 GHz was applied to several antennas 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 voltage of tuneable amplitude. The substrate bias was regulated using an RF power supply operating at 13.5 MHz. The DLC films were 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: $^{15}\text{N} + ^1\text{H} \rightarrow ^{12}\text{C} + ^4\text{He}\gamma$ rays, 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 ~ 8 nm thick. With increasing plasma pressure the distribution of the hillocks becomes random and more dense while the probability of the basket-like cluster formation significantly decreases. The XPS data taken at decreasing emergence angles show that the structure of the hillocks is dominated by sp^3 bonded carbon. The XPS argon signal disappears at 10° emergence angle indicating that integration of argon occurs mainly within the sp^2 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.

This work has been funded in the framework of the European Community Brite-EuRam Contract N° BRPR-CT98-0749.

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. Katsuno, S. Nitta and H. Habuchi* Dept. of Electrical Engineering, Gifu University, Gifu, JAPAN. *Dept. of Electrical Engineering, Gifu National College of Technology, Motosu, 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_x films have high resistivity, so it is difficult to obtain photocurrent. But photocurrent of a-CN_x increase from 2 eV to 6.2 eV, so it is easy to obtain CPM spectra at high photon energy region. CPM is obtained by dc measurements. We prepared a-CN_x made by a nitrogen radical sputtering method and by the layer-by-layer method having high photoconductivity [1]. Absorption coefficient α spectra of a-CN_x are obtained from the inverse of photon number 1/F of CPM spectra,

PDS spectra and that of transmittance spectra. The absorption coefficient α spectra of a-CN_x show starting of band edge at 2 eV and saturated at 3 eV. Then α spectra increase again at 3.5 eV up to 5.6 eV, which is showing another band edge appears at 3.5 eV. These spectra of α are very similar to photoconductivity spectra of a-CN_x. Urbach energy E_u obtained from PDS and CPM are 155 meV and 140 meV respectively. We will discuss two increase of absorption coefficients using a model of density of electronic states (DOS). We also discuss the data of ac-CPM comparing with dc-CPM.

[1] T. Katsuno et al., MRS Proc.593, (1999) p.499.

2:15 PM W12.4

DIAMOND NANO-ELECTRONICS: THE SELECTIVE REMOVAL OF SURFACE/NEAR SURFACE HYDROGEN WITHIN CVD DIAMOND FILMS FOR THE FORMATION OF NANO-TRANSISTORS. Oliver Williams, Electronic Engineering, University College London, UNITED KINGDOM; Haitao Ye, Electronic Engineering, University College London, UNITED KINGDOM; Richard B. Jackman, Electronic Engineering, University College London, UNITED KINGDOM.

The recent realisation that surface/near-surface hydrogen within CVD grown diamond films creates p-type character within this region, has enabled new approaches for the realisation of diamond devices to be explored. For example, we have recently fabricated field-effect transistors in this form of diamond which display full turn-off and saturation characteristics, as well as high levels of transconductance. Whilst the origin of this form of conductivity remains unclear, we have formed structures that remain stable over a wide temperature range (100-500K). We have also shown that this effect is not confined to single crystal or polycrystalline films, but is also evident in relatively disordered nanocrystalline CVD diamond. This is intriguing, as carrier mobility values higher than normally associated with such a material can be recorded. We have explored the carrier transport within such films using low temperature Hall measurements and the results will be presented in this paper. It has also proved possible to pattern the conductivity through the use of focussed electron and ion beams, enabling transistor structures to be realised with the very high resolution offered by these well established tools. This exciting development will be discussed and nanocrystalline diamond transistor device characteristics presented.

2:30 PM W12.5

NANODEVICE FABRICATION ON HYDROGENATED DIAMOND SURFACE USING ATOMIC FORCE MICROSCOPE. Minoru Tachiki, Tohru Fukuda, Hokuto Seo, Kenta Sugata, Tokishige Banno, Hitoshi Umezawa and Hiroshi Kawarada, School of Science & Engineering, Waseda University, Tokyo, JAPAN, CREST, Japan Science and Technology Corporation (JST), JAPAN.

The properties of hydrogen-terminated (H-terminated) diamond surfaces contrast with those of oxygen-terminated (O-terminated) surfaces. The surface hydrogenation induces p-type surface conduction even in undoped diamond. The nm scale separation of H-terminated surface and O-terminated surface will produce new types of nanoscale surface quantum devices (single charge tunneling devices etc.). Recently, local anodization on H-terminated diamond surface was performed using a metal (Au, Rh, etc.) coated conductive atomic force microscope (AFM) cantilever by applying voltage bias to the sample surface [1,2]. Compared with other materials, hydrogenated undoped diamond has great advantages to fabricate the nanodevices using AFM-based fabrication process because it has a structure similar to SOI (silicon-on-insulator) without any extra isolation procedures like SIMOX (separation by implanted oxygen). Up to the present, local insulation (40-60 nm in line width) has been successfully achieved using AFM [1,2]. Fowler-Nordheim (F-N) tunneling has been observed across the locally anodized region with 60 nm line width. Based on this technology, the operation of 1 micron side-gate diamond metal-insulator-semiconductor field-effect transistors MISFETs is performed using anodized surface as a gate insulator. This FET operates in enhanced mode and field-effect modulation of channel current is successfully achieved by the side-gated MIS structure. Using the locally anodized double tunneling barrier and aforementioned side gate FET structure, fabrication and operation of single hole transistors are also demonstrated. In the Id-Vg characteristics, coulomb blockade oscillation is observed even at liquid nitrogen temperature (77K).

[1] M. Tachiki, T. Fukuda, K. Sugata, H. Seo, H. Umezawa, H. Kawarada, Appl. Surf. Sci. 159-160 (2000) 578.

[2] M. Tachiki, T. Fukuda, K. Sugata, H. Seo, H. Umezawa and H. Kawarada: Jpn. J. Appl. Phys. 39 (2000) 4631.

2:45 PM W12.6

NANO SCALE OXIDATION ON THE HYDROGEN-TERMINATED DIAMOND SURFACE FOR DIAMOND NANO TECHNOLOGY. K. Sugata, M. Tachiki, T. Fukuda, H. Seo, T. Banno, H. Umezawa and H. Kawarada, School of Science & Engineering, Waseda Univ,

Tokyo, JAPAN; CREST, Japan Science and Technology Corporation (JST), JAPAN.

The nm-scale 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 hydrophobicity. On the other hand, the O-terminated diamond surface exhibits insulating, positive electron affinity and hydrophilicity. The both surfaces are stable in the air and the properties maintain for a long time. This characteristic is specific to diamond surfaces 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 (001) surface by atomic force microscope (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 such as scan speed, bias and humidity, insulated line with 30nm in width is obtained using the tip coated by W_2C . 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 as cathode and water layer from the ambient on the sample surface work as electrolyte. We also applied AC bias modulation to oxidation process and significant enhancement of line width was achieved. Using this AFM oxidation process on the H-terminated diamond surface, we can create new nano scale technology based on diamond.

[1] M. Tachiki, T. Fukuda, K. Sugata, H. Seo, H. Umezawa, H. Kawarada, *Appl. Surf. Sci.* 159-160(2000) 578.

[2] M. Tachiki, T. Fukuda, K. Sugata, H. Seo, H. Umezawa, H. Kawarada, *Jpn.J.Appl.Phys.* 39 (2000) 4631.

[3] H. Sugimura, T. Uchida, N. Kitamura, H. Masuhara *J.Phys.Chem.* 98 (1994) 4352.

3:30 PM W12.7

RAMAN AND EELS STUDIES ON MICROCRYSTALLINE DIAMOND PREPARED IN A LOW PRESSURE INDUCTIVELY COUPLED PLASMA. Katsuyuki Okada, Shojiro Komatsu, Seiichi Matsumoto, National Institute for Research in Inorganic Materials, Tsukuba, JAPAN.

Microcrystalline diamonds with several hundred nm in diameter have been prepared in a 13.56 MHz low pressure inductively coupled CH_4/H_2 or $CH_4/CO/H_2$ plasma. The bonding structures were investigated by Raman spectroscopy and electron energy loss spectroscopy (EELS). Visible (514 nm) and UV (325, 244 nm) excited Raman spectra exhibit peaks at around 1150 cm^{-1} assigned to sp^3 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 excite the sigma state of both sp^2 - and sp^3 -bonded carbon. The high resolution EELS spectra show peaks at around 1100 cm^{-1} assigned to C-C stretching vibration of sp^3 bonding and at around 700 cm^{-1} corresponding to the bending vibration of sp^3 bonding. It is qualitatively agreement with the Raman spectra. Furthermore the quantitative analyses of sp^2 and sp^3 bondings are carried out by comparing the pi state at around 285 eV with the sigma state at around 291 eV in the EELS spectra.

[1] K. Okada et al., *J. Appl. Phys.* 88,1674(2000).

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 Auciello, 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 CH_4 -Ar- N_2 gas mixtures with increasing N_2 content exhibit increasing conductivity from from about $10^{-3}(\Omega\cdot cm)^{-1}$ to $150(\Omega\cdot cm)^{-1}$ for films grown with 1% to 20% nitrogen in the plasma. The effect of nitrogen incorporation on the morphology of UNCD films of the films has been studied using HRTEM, 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 25% N_2 or more is used. EELS and electron diffraction confirm that the grains in the films are phase-pure diamond, whereas the grain boundaries show a structure similar to amorphous carbon. Neither the grains or the grain boundaries show detectable nitrogen incorporation, although SIMS data indicate that the films contain up to 0.5 atomic % nitrogen. These results are compared to data related to film conductivity. From these studies, it is believed that the change in

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. Sumant, O. Auciello, D.M. Gruen, J. Birrell and J.A. Carlisle, Materials Science Division, Argonne National Laboratory, Argonne, IL; H.D. Espinosa and B.C. Prorok, Department of Mechanical Engineering, Evanston, IL.

Over the past few years, there has been rapid growth in the of MEMS technology field. The applications based on MEMS technology are evolving so rapidly and in so many diverse areas that there are ever increasing demands on the operating limits of MEMS 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 MEMS 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 -1mm) that prevent fabrication of ultrasmall MEMS components. We have recently demonstrated a novel 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 ~ 30 -40 nm). We have successfully demonstrated the fabrication of UNCD-based MEMS components with a spatial resolution of 100 nm. In this paper, we will discuss detailed studies of the mechanical properties of UNCD coatings grown with and without nitrogen (N_2) 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.

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4:15 PM W12.10

NANOSTRUCTURED DIAMOND THIN FILMS ON Co-Cr-Mo WITH TiN INTERLAYER FOR BIOMEDICAL IMPLANT PURPOSES. Marc D. Fries and Yogesh K. Vohra, Department of Physics, University of Alabama at Birmingham, Birmingham, AL.

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, nanostructured diamond thin films are deposited on the metal articulating surfaces to protect against both chemical attack and physical abrasion. The Co-Cr-Mo alloy that comprises most implants 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 upon polished Co-Cr-Mo surfaces to act as a carbon diffusion barrier during deposition. TiN is well suited due 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.

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4:30 PM W12.11

DENSITY FUNCTIONAL BASED TIGHT BINDING STUDY OF C_2 AND CN DEPOSITION ON THE (100) DIAMOND SURFACE. Michael Sternberg, Thomas Frauenheim, Department of Physics, University of Paderborn, Paderborn, GERMANY; Peter Zapol, Larry A. Curtiss, Dieter M. Gruen, 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 C_2 dimers are the dominant growth species in hydrogen-poor argon plasmas. Recent experimental evidence shows that nitrogen addition to the plasma profoundly changes the morphology of the UNCD film. CN species are believed to play a major role in this case. Reactions of these molecules with unhydrided and monohydrided reconstructed diamond (100) surfaces were studied. A diamond growth mechanism by direct insertion of C_2 dimers into dimer rows of the unhydrided surface is proposed. A single CN prefers a one end attachment to a surface atom with its C

end down on the unhydrided (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. Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.