

SYMPOSIUM U

Amorphous and Nanostructured Carbon

November 29 – December 2, 1999

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* Invited paper

8:30 AM *U1.1

LARGE ARRAYS OF WELL-ALIGNED CARBON NANOTUBES. Z. F. Ren, Z.P. Huang, D.Z. Wang, J.G. Wen, Boston College, Dept of Physics, Chestnut Hill, MA; L. Calvet, J. Chen, J.F. Klemic, M.A. Reed, Yale University, Depts of Applied Physics, Elec. Eng. and Physics, New Haven, CT; J.H. Wang, SUNY-Buffalo, Dept of Chemistry, Buffalo, NY.

In this talk, we will present the recent results on growth and characterization of large arrays of well-aligned carbon nanotubes by plasma-enhanced chemical vapor deposition. In addition, we are also going to report our most recent success on the growth of single carbon nanotube on each nano-nickel dot in a pattern. With these carbon nanotubes, possible applications are discussed.

9:00 AM *U1.2

TIME-RESOLVED MEASUREMENTS OF CARBON NANOTUBE SYNTHESIS BY LASER ABLATION. David B. Geohegan, Alex A. Puretzky, Xudong Fan and Stephen J. Pennycook, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

The growth mechanisms of carbon nanotubes remain the subject of much controversy, principally due to the lack of *in situ* diagnostic investigations during synthesis. Pulsed laser vaporization is one of the best methods to synthesize high-purity single-walled carbon nanotubes (SWNT), and it is amenable to time-resolved characterization. We will present time-resolved imaging and spectroscopic measurements of the graphite/metal-catalyst ablation plume to understand how the hot laser plasma of initial ejecta (containing C, C₂, C₃, and metal catalyst atoms) is influenced by the high-pressure background gas (500 Torr Ar flowing inside a 2"-diameter tube) and hot oven (1000°C) to self-assemble SWNT. Gated-ICCD photography, optical emission spectroscopy, optical absorption spectroscopy, ion probes, laser-induced fluorescence (LIF) are first used to understand the kinetic energy and composition of the carbon species resulting from ablation of graphite in vacuum (relevant to amorphous diamond thin film growth). To study clustering in background gases, these techniques are combined with Rayleigh-scattering imaging and blackbody emission spectroscopy. These techniques are then applied under actual SWNT-synthesis conditions in order to measure catalyst-cluster and carbon-cluster nucleation times, the key temperatures and transport processes involved, and to identify the species responsible for nanotube growth. Imaging and spectroscopy is applied up to several seconds after laser ablation to track the globular plume as it propagates many centimeters inside the 2" tube. Bright-field TEM is used to characterize the raw soot collected from different positions in the chamber for correlation with the *in situ* imaging. Ex situ analysis by Z-contrast TEM and EELS is used to image and compositionally analyze catalyst nanoparticles which elude bright-field TEM. These ex situ measurements are used to infer SWNT growth rates and mechanisms. The goal of the research is twofold: to determine ways to control the length and purity of CNTs for molecular electronic applications, and to find ways to scale-up the SWNT-synthesis process for high-volume structural applications. This research was sponsored by the Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp., for the U.S. Department of Energy, under contract DE-AC05-96OR22464.

9:30 AM *U1.3

FORMATION MECHANISM OF SINGLE-WALL CARBON NANOTUBES. Masako Yudasaka, Fumio Kokai, Kunimitsu Takahashi, Shunji Bandow, Toshihiko Ichihashi, and Sumio Iijima; ICORP-JST, NEC, Tsukuba, JAPAN; IRI, Kashiwa, JAPAN; Meijo Univ, Nagoya, JAPAN.

We compared the formation of single-wall carbon nanotubes by Nd:YAG laser ablation, CO₂ laser ablation, and DC arc discharge using targets containing more than 95% C and less than 5% transition metals and/or Y. The graphite particles at the target surface melted and changed to a-C in Nd:YAG laser ablation, while they sublimed in CO₂ laser ablation and arc discharge. SWNTs, a-C, graphitic carbon, and C₆₀ were formed by Nd:YAG laser ablation. Similar components were formed in arc discharge but the quantity of C₆₀ was much less in the arc discharge. CO₂ laser ablation produced nanohorn aggregates and SWNTs (1,2). The metal tended to remain and accumulate on the target surface in Nd:YAG laser ablation, but it evaporated almost completely in the other two methods. SWNTs could be formed when the ambient temperature was above 1100 K in the Nd:YAG laser ablation, while they could be formed at and above room temperature in the other two methods. In situ observation of the emission spectra showed that the high-density area formed in front of the target lasted

for 5 μs or more. The same observations in the CO₂ ablation showed that the high-density region did not appear; instead, the emitted carbon species forming a mushroom-like cloud did (3). Based on these and other results (4), we discussed the influence of metal and carbon species on SWNT formation and inferred the SWNT formation mechanism. References: (1) S. Iijima, Chem. Phys. Lett. in press. (2) M. Yudasaka et al, J. Phys. Chem. B 103, 3576 (1999). (3) F. Kokai et al, J. Phys. Chem. B 103, 4346 (1999). (4) M. Yudasaka, et al.: J. Phys. Chem. B 102, 4892 (1998); J. Phys. Chem. B 102, 10201 (1998); Chem. Phys. Lett. 299, 91 (1999).

10:30 AM U1.4

MAKING MULTIWALLED CARBON NANOTUBES USING HEAT TREATMENT METHODS. A.A. Setlur, GE Corporate Research and Development, Schenectady, NY; S.P. Doherty and R.P.H. Chang, Northwestern University, Dept. of Materials Science and Engineering, Evanston, IL.

One of the main limitations in using carbon nanotubes as a material in many applications is the inability to make large scale quantities of high quality nanotubes. Scalable production of carbon nanotubes may require moving away from typical arc discharge and laser ablation synthesis methods, which have been very successful in producing research quantities of nanotubes. We have developed new methods to make multiwalled nanotubes by controlling the heat treatment and graphitization of fullerene soot. These nanotubes are similar in length, diameter, and morphology to nanotubes made using the carbon arc. While a heat treatment process could be amenable to large scale production of nanotubes, the carbon arc is still necessary to produce the starting materials for this synthesis. Consequently, we have been investigating the heat treatment of other carbon materials to see if it is possible to make nanotubes using inexpensive precursors. By controlling the kinetics of the graphitization process, it is possible to make multiwalled nanotubes by the high temperature heat treatment of common non-graphitizable carbons. It is important to note that these methods do not need metal particles to catalyze nanotube growth. These experiments could give opportunities to develop scalable methods to make multiwalled nanotubes as well as understand possible mechanisms for nanotube growth.

10:45 AM U1.5

MOLECULAR BEAM EPITAXY SYNTHESIS OF CARBON NANOTUBES. Frank Tsui and Paul Ryan, University of North Carolina, Dept of Physics and Astronomy, Chapel Hill, NC.

Single-walled carbon nanotubes (SWNT) have been synthesized using molecular beam epitaxy (MBE) techniques. Epitaxial Mo islands grown on sapphire substrates were used as the catalytic templates. Nucleation and growth of SWNT were studied in-situ using real-time reflection high energy electron diffraction (RHEED) and scanning probe microscopy (SPM). Our studies indicate that the nucleation of SWNT is preceded by the formation of periodic carbide structures, and that the diameters of the SWNT were determined by the carbide structures. The observed growth process for SWNT is consistent with the root growth mechanism.

11:00 AM U1.6

SYNTHESIS AND GROWTH MECHANISMS OF MULTIWALLED NANOTUBES. David Jacques, Stephane Villain, Apparao Rao, Rodney Andrews, Frank Derbyshire, Center for Applied Energy Research, University of Kentucky, Lexington, KY; Elizabeth Dickey, Dali Qian, Chemical and Materials Engineering, University of Kentucky, Lexington, KY.

In a recent publication we have described the synthesis of multiwalled carbon nanotubes (MWNTs) by the reaction of a hydrocarbon vapor over a dispersed iron catalyst that is deposited on quartz substrates¹. The usual system configuration involves entraining a mixture of xylene and ferrocene into an inert gas stream. The mixture flows into a quartz tube furnace in which are placed quartz plates to provide additional substrate area. Decomposition of the ferrocene at temperatures in the range 625-775 C, and at atmospheric pressure, produces a coating of iron nanoparticles on the quartz surfaces, and these metal sites function as catalysts for the formation and growth of MWNTs. On flat substrates, the MWNTs grow perpendicular to the substrate in parallel alignment, forming thick mats that can be readily harvested. We have now extended this work to examine the effect of a number of operating parameters on MWNT yield, purity, and other characteristics (diameter distribution, length). These parameters include the feed injection temperature, furnace temperature, hydrocarbon partial pressure, reaction time, space velocity, and iron to carbon ratio in the feed. Under selected conditions, we have found that it is possible to produce essentially pure MWNTs, with little or no amorphous carbon, and to greatly increase the yield (approaching 60% carbon yield). Characterization of the MWNTs by electron microscopy has shown that there is a relationship between metal particle size and MWNT diameter. Using

these new findings, we have refined a model to help to account for the growth mechanism of MWNTs, and to account for the experimental data. ¹R. Andrews et al., Chem Phys Lets, 303 (1999) 467-474.

11:15 AM U1.7

SYNTHESIS OF C₆₀ CHAINS CONTAINED WITHIN CARBON NANOTUBES. Brian W. Smith, David E. Luzzi, University of Pennsylvania, Dept of Materials Science and Engineering, Philadelphia, PA.

We have discovered self-assembled chains of C₆₀ inside single wall carbon nanotubes. These belong to a new, complete class of hybrid materials: single wall nanotubes containing hemispherically-capped graphene cylinders of various lengths, the set of which is described by C_{60+10n} where $n \geq 0$. Certain encapsulated structures exist as metastable configurations due to the geometric constraints imposed by the surrounding tube. Using both *in situ* and *ex situ* experiments, we show the synthesis of such fullerene hybrids, and we discuss the mechanisms by which this synthesis occurs. Not only could these materials have useful properties themselves, but also we present two novel applications of nanotubes demonstrated by this work: as nanoscopic chemical reaction chambers, and as supports for the isolation and imaging of individual organic molecules.

11:30 AM U1.8

DENSE ARRAYS OF WELL-ALIGNED CARBON NANOTUBES COMPLETELY FILLED WITH SINGLE CRYSTALLINE TITANIUM CARBIDE WIRES ON TITANIUM. Y. Gao, J. Liu, M. Shi and S. H. Elder, Pacific Northwest National Laboratory, Richland, WA.

We have synthesized dense and uniform arrays of well-aligned carbon nanotubes on titanium substrates over large areas, in which all the tubes are simultaneously and completely filled with single crystals of titanium carbide. The carbon nanotubes were synthesized by thermal chemical vapor deposition of ethylene on iron-coated substrates, while the titanium carbide was simultaneously formed inside the nanotubes through a simultaneous solid state reaction. A base dissolution and precipitation mechanism was proposed for the growth of titanium carbide filled carbon nanotubes. Growth of oriented and filled carbon nanotubes requires stable catalytic particles and low free energy of formation of a reaction product in the core. Thus, the same method can be used to fabricate oriented nanotube arrays filled with other carbides on a variety of substrates over large scale. Such well-aligned and densely packed uniform carbon nanotubes, completely filled with nanowires on conducting substrates, will have great potential in many applications.

11:45 AM U1.9

SINGLE- AND MULTI-WALLED BORON NITRIDE NANOTUBES PRODUCED FROM CARBON NANOTUBES BY A SUBSTITUTION REACTION. Yoshio Bando, Dimitri Golberg, Weiquang Han, Keiji Kurashima, Tadao Sato, National Institute for Research in Inorganic Materials, Tsukuba, JAPAN.

A new method involved carbon nanotubes substituted reaction was developed for the synthesis of mass quantities of boron nitride nanotubes. Single- and multi-walled boron nitride (BN) nanotubes have been produced by a thermal treatment of a mixture of boron trioxides and carbon nanotubes at 1500-1750K in a nitrogen flow. The nanotubes thus prepared were characterized by high resolution TEM and EELS under a 300kV field emission TEM. The diameter of single wall nanotubes in the resultant bundles was 1.2-1.4nm, which was similar to the diameter of the starting carbon nanotubes. The multi-walled BN nanotubes revealed perfect straight shapes, limited number of shells (typically 2-6) and remarkable ordering of the graphite-like sheets in the so called non-helical zig-zag fashion along the tube axis. It is proposed that carbon atoms of carbon nanotubes can be fully substituted by boron and nitrogen atoms through a general chemical reaction. Using the same substitution reaction method, multi- and single-walled B-doped carbon and B/N-doped carbon nanotubes were also synthesized.

SESSION U2: STRUCTURE AND CHARACTERIZATION OF NANOTUBES

Chairs: Mildred S. Dresselhaus and John E. Fischer
Monday Afternoon, November 29, 1999
Room 311 (H)

1:30 PM *U2.1

STRUCTURE OF SELF-ORGANIZED SWNT: A TEM STUDY. Annick Loiseau, LEM UMR Onera-Cnrs, Chatillon FRANCE; L. Henrard, University, Namur, BELGIQUE; P. Bernier, GDPC, Cnrs, Montpellier, FRANCE; C. Journet, MPI, Stuttgart, GERMANY.

We present a TEM study of electric-arc produced single-wall carbon nanotube bundles, combining HRTEM images and quantitative electron diffraction. Analyses are done with the help of simulations based on the dynamical theory. We show that these techniques provide a direct and quantitative analysis of the lattice parameters of the tube packing and of the distribution of the single-wall nanotube chiralities. We stress the importance of the twist of the bundles and of the fact that bundles may be composed of tube packings differently oriented with respect to the bundle axis, in the interpretation of our data. We show that, within a given bundle, no chirality is favoured whereas the diameters of individual nanotubes are almost uniform. On the contrary, isolated tubes display much dispersed diameters.

2:00 PM U2.2

DIRECT OBSERVATION OF TIME AND SPATIAL EVOLUTION IN THE FULLERENE CAGE FORMATION PROCESS. Shinzo Suzuki, Toshimitsu Ishigaki, Daisuke Kasuya and Yohji Achiba, Tokyo Metropolitan Univ, Dept of Chemistry, Tokyo, JAPAN; Hiromichi Kataura, Tokyo Metropolitan Univ, Dept of Physics, Tokyo, JAPAN.

Laser ablation of graphite in rare gas atmosphere gives rise to the formation of carbon clusters and particles. Under a particular condition such as high pressure (100-500 Torr) and high temperature (600C-1400C), the ablation process results in the formation of fullerenes and carbon nanotubes. The yields of fullerenes and nanotube were found to be much dependent on the ambient condition. In the present work, we will show the direct observation of time and spatial evolution of fullerene cage network formation by detecting the emission by a high speed video camera as well as an ICCD detector. The emission properties were examined under various conditions and directly compared with the yields of fullerenes and carbon nanotubes. As a result, it was found that the prolonged emission observed in the ms time range is strongly related with the heat of the formation of the fullerene network formation.

2:15 PM U2.3

TWISTING OF SINGLE-WALLED CARBON NANOTUBE BUNDLES. Lu-Chang Qin, Sumio Iijima JST-ICORP Nanotubulite Project, Tsukuba, JAPAN.

Single-walled carbon nanotubes form raft-like bundles when they are produced by laser evaporation of graphite. Many of the bundles twist to give rise to a rope-like structure instead of forming aligned parallel bundles. This phenomenon has been found to be common and it provides interesting insights on the mechanical properties of carbon nanotubes. High-resolution transmission electron microscopy has been used to study the twist structure and the twisting of the bundles of single-walled carbon nanotubes. Bonding analysis suggests that the total energy of the twisted rope-like structure would be lower when the tubules are helical and they have different helicities among the individual tubules within the bundle. The twisting is suggested to accommodate the local bonding between the neighboring tubules in order to lower the total energy of formation. The pitch length of a rope-like bundle has also been measured to deduce the twisting angles. Using the experimentally obtained data, some of the mechanical properties such as stability and strength of single-walled carbon nanotube bundles have been studied as well.

2:30 PM U2.4

STRUCTURE AND DYNAMICS OF ROPES OF SINGLE-WALL CARBON NANOTUBES - NEUTRON SCATTERING STUDIES. Zdenek Benes, John E. Fischer, University of Pennsylvania, Dept of Material Science, Philadelphia, PA; Peter Papanek, University of Pennsylvania/NIST, Gaithersburg, MD.

Structure and lattice dynamics of bulk samples single-wall carbon nanotube ropes (SWNT) are studied using X-ray and neutron diffraction and inelastic neutron scattering techniques. From the diffraction profiles we obtain information about rope structures, tube diameter distribution, and the amount of residual catalyst and graphitic impurities present in our samples. Filter-analyzer neutron spectroscopy and time-of-flight spectroscopy are used to measure the phonon densities of states. The results for samples produced by two different methods - laser ablation (Rice) and arc discharge (Montpellier) - are analyzed and compared.

2:45 PM U2.5

ELASTIC AND INELASTIC NEUTRON SCATTERING STUDIES OF THE STRUCTURE AND DYNAMICS OF NANOBUNDLES OF SINGLE WALL CARBON NANOTUBES. Stephane Rols, Eric Anglaret, Jean-Louis Sauvajol, Groupe de Dynamique des Phases Condensees, Universite Montpellier II, Montpellier, FRANCE.

Elastic and inelastic neutron scattering are used to study the structure and dynamics of single wall-carbon nanotubes (SWNT) self-assembled into nanobundles (NBSWNT). Neutron diffraction is used as a useful tool to study the structure of both the SWNT and

NBSWNT. Calculations on finite-size bundles are compared to the data in order to estimate the distribution of tube diameters. We present time of flight inelastic scattering measurements of the phonon density of states and discuss the main features of the spectra in the light of Raman experiments and calculations on NBSWNT. At low frequencies, we observe a peculiar shape of the density of states that we assign to contributions of low frequency intratube and intertube excitations. We discuss the peculiar temperature dependence of the low frequency density of states in terms of anharmonicity, structural disorder and electron-phonon interactions.

3:30 PM *U2.6

RESONANCE RAMAN SPECTROSCOPY OF SINGLE WALL CARBON NANOTUBES. M.S. Dresselhaus^{a,c}, S.D.M. Brown^a, P. Corio^a, A. Marucci^a, M.A. Pimenta^b, G. Dresselhaus^d, K. Kneipp^{e,f}; ^aDepartment of Physics, Massachusetts Institute of Technology, Cambridge, MA; ^bDepartamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, BRAZIL; ^cDepartment of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA; ^dFrancis Bitter National Laboratory, Massachusetts Institute of Technology, Cambridge, MA; ^eSpectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge, MA; ^fPhysics Department, Technical University of Berlin, Berlin, GERMANY.

The unique properties of the resonance Raman spectra of carbon nanotubes using laser excitation energies E_L in the range of 1.58eV to 2.71eV are discussed in terms of resonant enhancement associated with singularities in the 1D electronic density of states. The dominant features of the first-order Raman spectrum are the radial breathing modes ($\sim 150\text{ cm}^{-1}$) and the tangential modes at $\sim 1600\text{ cm}^{-1}$, each having unique spectral features and each having overtones and combination modes. Asymmetries between the Stokes and anti-Stokes spectra are demonstrated and their interesting dependence on E_L are explained. Surface-enhanced Raman spectroscopy using colloidal fractal silver clusters as the surface-enhancement medium provide a means for enhancement of the Raman signal by many orders of magnitude, thereby facilitating the observation of the Raman spectrum of a small number of SWNTs, perhaps ultimately only a single nanotube.

4:00 PM U2.7

BUNDLE EFFECT ON THE OPTICAL PROPERTIES OF SINGLE-WALLED CARBON NANOTUBES. Hiroichi Kataura, Yutaka Maniwa, Tokyo Metropolitan Univ, Dept of Physics, Tokyo, JAPAN; Shinichi Masubuchi, Shigeo Kazama, Chuo Univ, Dept of Physics, Tokyo, JAPAN; Yohsuke Ohtsuka, Shinzo Suzuki and Yohji Achiba, Tokyo Metropolitan Univ, Dept of Chemistry, Tokyo, JAPAN.

Theoretical calculations have predicted that inter-tube interaction in bundle of single-walled carbon nanotube (SWNT) modifies the electronic band structure. To see the bundle effect, we used a doping-dedoping technique. It is well known that bromine doped SWNT bundles show large frequency shift of breathing mode due to the charge transfer, and that they are stable even under the vacuum at room temperature. On the other hand, bromine molecules around individual SWNTs would be removed by the evacuation since there is no stable site. Most of samples are constructed with both types, bundles and individual SWNTs. Thus, it is expected that the resonance Raman scattering of partially doped bundle and undoped individual SWNTs can be measured simultaneously using evacuated sample after full doping. Indeed, we observed two breathing mode bands that show quite different resonance feature from each other. In this presentation, a difference in resonance effect between SWNT bundles in pristine sample and individual SWNTs in doped sample will be discussed. We also prepared many kinds of SWNTs using variety of metal catalysts and synthesis parameters. Then we successfully got some samples of different bundle size with the same diameter distributions. Results about optical absorption and resonance Raman scattering will be discussed.

4:15 PM U2.8

ON THE RAMAN SPECTRUM OF SINGLE WALL CARBON NANOTUBES. S. Rols, J.L. Sauvajol, L. Alvarez and E. Anglaret GDPC, University Montpellier, Montpellier, FRANCE.

Raman investigations have been performed on various samples of single wall carbon nanotubes prepared from laser ablation and electric arc discharge technique. We correlate the tube average diameter and diameter distribution derived from the analysis of the neutron diffraction spectrum with the profile of the Raman spectrum in the A_{1g} breathing modes (the R modes). In this aim the R mode frequency of SWNT bundles were calculated. In the high frequency range, we state that the change in the profile of the graphite-like modes with the incident excitation energy can be understood in terms of dominant metallic or semiconducting contributions. Especially the evidence of a Breit-Wigner-Fano lineshape for the graphite-like modes

is the sign of a metallic phase in resonance with the energy excitation. In the intermediate frequency range two distinct Raman spectra assigned to semiconducting SWNT bundles with tubes of large and small diameters respectively are evidenced.

4:30 PM U2.9

RESONANCE RAMAN AND SURFACE-ENHANCED RESONANCE RAMAN SPECTROSCOPY OF CARBON NANOTUBES. S.D.M. Brown^a, P. Corio^a, A. Marucci^a, K. Kneipp^c, M.A. Pimenta^d, M.S. Dresselhaus^{a,b}; ^aDepartment of Physics, Massachusetts Institute of Technology, Cambridge, MA. ^bDepartment of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA; ^cDepartment of Physics, Technical University, Berlin, GERMANY; ^dDepartamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, BRAZIL.

We have performed Raman spectroscopy (RS) and Surface-Enhanced Raman Spectroscopy (SERS) on carbon nanotubes at various excitation wavelengths. In the Raman spectra measured at laser excitation energies $E_L > 2.2\text{ eV}$ and $E_L < 1.84\text{ eV}$, the tangential phonon mode region shows contributions at 1600 cm^{-1} , 1590 cm^{-1} and 1560 cm^{-1} . These Raman lines have been attributed to the semiconducting nanotubes. In the narrow excitation window between 2.2 eV and 1.84 eV, additional phonon modes at 1580 cm^{-1} , 1540 cm^{-1} and 1515 cm^{-1} , appear in the Raman spectra. These modes are attributed to the resonantly enhanced phonon modes of the metallic carbon nanotubes in the sample. To perform the surface-enhanced Raman studies, we used a SERS substrate of metal islands films, produced through the evaporation of gold (film thickness 50 Å) or silver (film thickness 100 Å and < 50 Å). SERS studies performed on carbon nanotubes adsorbed on these films using excitation energies $E_L > 2.2\text{ eV}$ and $E_L < 1.84\text{ eV}$ show that the shape of the Raman band for the semiconducting nanotubes are largely unaffected by the presence of the metal island films and consists of the same contributions at the same relative intensities as in normal Raman scattering (RS). In the narrow excitation window between 2.2 eV and 1.84 eV, however, the contribution of the phonon modes for the metallic nanotubes compared to phonon modes for the semiconducting tubes is much more pronounced than in the case of RS. This indicates stronger surface enhancement for metallic phonon modes than for semiconducting ones, which might be explained by a stronger interaction of the metal islands films with the metallic nanotubes than with the semiconducting nanotubes. The MIT authors gratefully acknowledge support by NSF Grant DMR-98-04734.

4:45 PM U2.10

13C NMR INVESTIGATIONS OF CARBON NANOTUBES. C. Goze, S. Latil, L. Vaccarini, P. Gaveau, V. Micholet, R. Aznar, P. Bernier, GDPC UM2, Montpellier, FRANCE; P. Petit, C. Matthis, ICS, Strasbourg, FRANCE; Y. Fagot, M. Mehring, Physikalisches Institut, Stuttgart, GERMANY; A. Rubio, Valladolid University, Valladolid, SPAIN; K. Metenier and F. Beguin CRMD, Orléans, FRANCE.

In this talk we report on a Nuclear Magnetic Resonance study of pristine and intercalated single wall carbon nanotubes. 10% ^{13}C enriched SWNT were synthesized in order to improve the NMR signal to noise ratio. The raw sample was purified and characterized by electron microscopy and X ray diffraction. We will present and discuss the temperature dependence of the NMR spectra and relaxation rates in terms of molecular dynamics and electronic contributions. In particular, we observe a drastic change in the ^{13}C relaxation rates after doping. NMR of the alkali indicates a charge transfer to the nanotube. For example, we found it to be quasi total in the case of Li. We will focus on the metallic behavior to interpret our NMR results.

SESSION U3: ELECTRONIC AND MECHANICAL PROPERTIES OF NANOTUBES

Chairs: Walt A. de Heer and Apparao M. Rao
Tuesday Morning, November 30, 1999
Room 311 (H)

8:30 AM *U3.1

QUANTIZED CONDUCTANCE AND MECHANICAL PROPERTIES OF MULTI WALLED CARBON NANOTUBES. Walt A. de Heer, Philippe Poncharal, Z.L. Wang, School of Physics, Georgia Institute of Technology, Atlanta, GA.

In situ electron microscopy experiments and scanning probe experiments on MWNT's have demonstrated that they are quantized conductors at room temperature ($G=1\text{ G}_0$)[1], implying that the current only flows over the outer surface of the NT (as recently confirmed in other experiments[2]), and long coherence lengths. The effect has been demonstrated using liquid metal contacts on about 80 samples, of which the vast majority demonstrate the effect after

appropriate conditioning. Mechanical properties are probed by exciting mechanical resonances in selected nanotubes[3], which demonstrate that the stiffness of the tubes reduces with increasing tube diameter due to the emergence of a buckling-like mode. Recent in situ experiments on NT field emission and damage will be discussed.

1. S. Frank, P. Poncharal, Z. Wang, W.A. de Heer, Science 1998, 280, 1744.
2. A. Bachtold, C. Strunk, J. Salvetat, J. Bonard, L. Forro, T. Nussbaumer, C. Schonenberger, Nature 1999, 397, 673.
3. P. Poncharal, Z. Wang, D. Ugarte, W.A. de Heer, Science 1999, 283, 1513.

9:00 AM *U3.2

ATOMIC TRANSFORMATIONS AND QUANTUM TRANSPORT IN CARBON NANOTUBES. J. Bernholc, M. Buongiorno Nardelli, J.-L. Fattebert, D. Orlikowski, R. Roland and Q. Zhao, NC State University, Raleigh, NC.

High strain conditions can lead to a variety of atomic transformations in nanotubes, which usually occur via successive bond rotations. The energetic barrier for the rotation is dramatically lowered by strain, and ab initio results for its strain dependence will be presented. While very high strain rates must lead to tube breakage, (n,m) nanotubes with $n, m < 14$ can display plastic flow under suitable conditions. This occurs through the formation of a 5-7-7-5 defect, which then splits into two 5-7 pairs. The index of the tube changes between the 5-7 pairs, potentially leading to metal-semiconductor junctions. A different way to induce nanotube transformations is through addimers, which incorporate into the hexagonal structure under strain. In zigzag tubes, addimer-induced transformations can again lead to index changes and the formation of metallic quantum dots in a semiconducting nanotube. The defects and the index changes occurring during the above mechanical transformations also affect the electrical properties of nanotubes. We have computed the quantum conductances of strained tubes, defects, and nanotube junctions using both tight binding and ab initio methods. The results show that the defect density and the contacts play key roles in reducing the conductance at the Fermi energy. We also explored the role of bending in changing the electrical properties and found that mechanical deformations affect differently the transport properties of achiral and chiral nanotubes. Our results are in good agreement with recent experimental data.

9:30 AM U3.3

ELECTRONIC STRUCTURES OF SINGLE-WALLED CARBON NANOTUBES STUDIED BY NMR. X.-P. Tang, A. Kleinhammes, H. Shimoda, L. Fleming, O. Zhou, Y. Wu, University of North Carolina, Dept of Physics and Astronomy, Chapel Hill, NC.

The novel structure of single-walled carbon nanotubes (SWNTs) leads to fascinating electronic properties and many potential microelectronic devices have been proposed based on such properties. Two types of SWNTs have been predicted with 1/3 being metallic and 2/3 being semiconducting, depending on the diameter and the chirality of the nanotube. Measurements of individual tubes confirm qualitatively this prediction. However, most SWNTs produced by laser ablation or arc-discharge form bundles of close-packed tubes and theory predicts that tube-tube interactions in such bundles could affect the electronic properties significantly. Here we report a ^{13}C NMR study of the electronic structures of SWNTs. Spin lattice relaxation is employed to measure the density of states at the Fermi level $g(E_F)$. The ability of NMR in measuring $g(E_F)$ is based on the fact that the nuclear spin-lattice relaxation rate, $1/T_1$, is proportional to $g(E_F)^2$ in metallic systems. An advantage of NMR versus other techniques used for measuring $g(E_F)$ is that NMR probes the local density of states. Thus, different types of nanotubes can be studied selectively. We found that indeed there are two types of SWNTs. One third of SWNTs have a density of states at the Fermi level very close to the theoretically predicted value for the metallic tubes. The other two thirds of the tubes have a much smaller density of states at the Fermi level. However, both types of tubes exhibit metallic character where the spin-lattice relaxation rate is proportional to the temperature. This indicates that tube-tube interactions could indeed alter the electronic properties of SWNTs. The NMR method also offers a convenient way of characterizing the influence of various sample preparation and processing conditions on the electronic properties of SWNTs.

9:45 AM U3.4

NMR STUDY OF SINGLE WALL CARBON NANOTUBES. Hironori Ogata, Institute for Molecular Science, Okazaki, JAPAN; Shunji Bandow, Nanotubulites Project, JST-ICORP, JAPAN; Shogo Kuno, Yahachi Saito, Dept of Electrical and Electronic Eng, Mie Univ, JAPAN.

^{13}C NMR studies of single wall carbon nanotube (SWNT), which was produced by the Rh-Pt catalyst and purified by the oxidation

technique using H_2O_2 , are reported. Temperature dependence of ^{13}C spin lattice relaxation time, T_1 , shows a Korringa-like behavior ($T_1 T = 950(\text{K sec.})$), at 9.39T in the temperature region between 5 K and 100 K. This fact suggests that metallic SWNTs exist in the sample at 9.39 T. The field dependence of T_1 for this sample is also discussed.

10:30 AM U3.5

TUNING THE ELECTRONIC STRUCTURE OF CARBON SINGLE WALL NANOTUBES. Pierre Petit, Claude Mathis, Inst Charles Sadron, Strasbourg, FRANCE; Patrick Bernier, GDPC, Montpellier, FRANCE.

In this communication we report the possibility of tuning the Fermi level of single wall carbon nanotubes upon chemical doping. The doping process used allows to fill or deplete selectively the density of states of the different kind of tubes (semiconducting and metallic) that constitute the material, and consequently to control their electronic structure. The modifications of the electronic structure of SWNT induced by the doping are directly monitored by optical absorption spectroscopy performed on thin films. The same doping process has been performed on the bulk material and the variation of the resistivity versus the chemical composition is reported.

10:45 AM U3.6

THE ELECTRONICS OF KINKED CARBON NANOTUBES. Daniel Tekleab, Richard Czerw, Clemson University, Dept of Physics and Astronomy, Clemson, SC; P.M. Ajayan, Rensselaer Polytechnic Institute, Dept of Materials Science and Engineering, Troy, NY; D.L. Carroll, Clemson University, Dept of Physics and Astronomy, Clemson, SC.

The electronic structure of mechanically deformed multi-wall nanotubes (MWNT) has been investigated using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). Variations in electronic structure along the body of kinked tubes occur at several length scales. Near kinking deformations, a strong suppression of the LDOS in the valence band is observed. At 50 nm away from the kinked region, effects of the deformation can still be observed in the electronic structure, while further from the kinked region (> 200 nm) the LDOS is that of an undisturbed MWNT. We have correlated these variations in LDOS with variations in contact potential formed between the tube and the substrate. We show that tube deformation plays a major role in the formation of contact resistance for MWNTs.

11:00 AM U3.7

ADDIMERS ON STRAINED CARBON NANOTUBES: A NEW ROUTE FOR QUANTUM DOT FORMATION. Daniel Orlikowski, Marco Buongiorno Nardelli, Jerry Bernholc and Christopher Roland, Department of Physics, NC State University, Raleigh, NC.

Using large-scale molecular dynamics simulations, we have investigated the effects of adatoms and addimers on strained carbon nanotubes. Most important, addimers on nanotubes under tension lead to the formation of a new 7-5-5-7 defect that spontaneously transforms itself into other extended defect structures, that ultimately wrap themselves about the circumference of the nanotube. These defects are actually short segments of a tube with a changed helicity, which suggests that the combination of of addimers plus strain may be used to form nanotube-based quantum dots. The simulations show that the formation of such structures is particularly clean and promising for the (n,0) zigzag tubes, where the presence of addimers selectively induces plastic transformations on tubes that are otherwise brittle. The formation energies, activation energies, electronic properties, STM images and transport properties on the induced defects and their associated transformations will all be discussed.

11:15 AM U3.8

EFFECTS OF STRAIN ON THE RESISTANCE OF CARBON NANOTUBES. S. Paulson, M.R. Falvo, N. Snider, R. Superfine, S. Washburn, University of North Carolina-Chapel Hill, Dept of Physics and Astronomy; A. Helsen, A. Seeger, R.M. Taylor II, UNC-CH, Dept of Computer Science, Chapel Hill, NC.

We have used an advanced interface to an Atomic Force Microscope to probe the effects of mechanical strain on the transport properties of carbon nanotubes. The tip can strain the nanotubes in two distinct ways. By pressing on top of the tube, a small region is deformed radially, while the rest of the tube is undisturbed. Alternately, the tube can be pushed laterally, with the ends fixed (by the metal leads) resulting in a nearly uniaxial tensile strain. Experiments on both Multi-walled and Single-Walled nanotubes have been performed, and in the case of lateral pushing, enough strain to fracture the tubes was applied. The effects of strain will be compared to theoretical results, and finally the spectroscopy of the rejoined ends of broken nanotubes will be discussed.

11:30 AM U3.9

EFFECT OF GAS ADSORPTION ON THE ELECTRICAL PROPERTIES OF SINGLE WALLED CARBON NANOTUBES MATS. Christian Marliere, Laboratoire des Verres, Univ. Montpellier 2, Montpellier, FRANCE; Ahmed Zahab, Laetitia Vaccarini, Groupe de Dynamique des Phases Condensees, Univ. Montpellier 2, Montpellier, FRANCE.

In this paper we report on the first observation of SWNT mats electrical conductivity variations occurring during the adsorption or desorption of gases. Single wall nanotubes were made by the arc-discharge method [1]. Residual impurities (fullerenes, amorphous carbon, catalyst metals...) were removed by tangential filtration process followed by high temperature annealing under vacuum [2]. Electrical conductivity measurements using a four-probe contact pressure method were performed at room temperature. The samples were carefully outgassed and kept under high-vacuum conditions in the experimental chamber. In a first step we proceed to a fast introduction of high purity gas ($P=1\text{atm}$). During this operation, a remarkable - and reversible - variations of the electrical conductivity of the samples has been observed. The amplitude and time constant (in the range of few minutes) of these phenomena exhibit a big dependence on the gaseous specie (H_2 , He, N_2 , Ar, O_2) introduced in the reactor and a good correlation to the kinetic diameter of the gas molecule. To better understand the basic processes involved in this new phenomenon more experiments are in progress and will be presented in this paper. [1] C. Journet et al. Nature, 388 (1997) p756. [2] L. Vaccarini et al. Synthetic Metals 101 (1999) in press.

11:45 AM U3.10

INTERACTION OF CARBON NANOTUBES WITH GRAPHITE SURFACES. R. Joshua Steele, Michael R. Falvo, Richard Superfine, Department of Physics and Astronomy, University of North Carolina at Chapel Hill, NC; Russell M. Taylor II, Department of Computer Science, University of North Carolina at Chapel Hill, NC.

While the mechanical properties of carbon nanotubes have been extensively investigated (such as buckling and young's modulus, for example), the interaction of the nanotubes with surfaces has yet to be thoroughly investigated. We present here the results of our research in this area. We show that multiwalled nanotubes have certain preferred orientations on graphite surfaces, which are due to lattice locking between the graphite lattice and the nanotubes. The forces required to move the nanotubes in these orientations (the only ones in which we see rolling) can be as much as 10 times the force required to move the nanotube out of the locked orientation. There is also strong evidence that these orientations are different for each nanotube, which suggests that chirality plays a part in the locking angles. We also present results from single walled nanotube (SWNT) and SWNT bundle experiments on graphite. In these experiments, we explore preferred orientations for SWNTs and bundles, as well as the length and diameter dependence of the structures on their rigidity.

SESSION U4: ELECTRON EMISSION FROM NANOTUBES AND AMORPHOUS CARBON
Chairs: William I. Milne and John Robertson
Tuesday Afternoon, November 30, 1999
Room 311 (H)

1:30 PM *U4.1

LOW THRESHOLD FIELD EMISSION FROM NANO-CLUSTERED CARBON FILMS. W.I. Milne, Cambridge University, Engineering Department, Cambridge, ENGLAND.

Recently there has been an increasing interest in finding suitable thin film materials for use as the cathode in tip free Field Emission Displays (FEDs). Hydrogenated amorphous carbon (a-C:H), tetrahedrally bonded amorphous carbon (ta-C), diamond, nanocluster coral-like films, polymers and nanotubes are amongst those studied to date. To complement this work we have carried out field emission measurements on a selection of nanocluster carbon films. The first series were produced at room temperature from the Cathodic Vacuum Arc system. The effect of helium partial pressure on film growth at different nitrogen partial pressure in the arc system has been studied. Film morphology from the mirror smooth (ta-C) through nanocluster (50 - 200 nm sizes) to fibrous type can be produced. The threshold field for emission varied from 1V/micron to 10 V/micron for an emission current density of 1mAcm^{-2} . Cluster assembled carbon films have also been produced from a supersonic cluster beam for comparison and these are also found to emit at fields of order 1V/micron. This paper will present a review of the above work and compare the results with work on going elsewhere.

2:00 PM *U4.2

FIELD EMISSION FROM DIAMOND AND CARBON NANOTUBES EMITTERS. Wei Zhu, G.P. Kochanski, S. Jin, Bell Labs, Lucent Technologies, Murray Hill, NJ; C. Bower, O. Zhou, University of North Carolina, Chapel Hill, NC.

I will describe the fabrication and physical properties of both diamond and carbon nanotube field emitters. While they differ significantly in the emission physics involved, both emit electrons efficiently at low electric fields and are capable of producing technologically meaningful current densities. I will show that defects in diamond are mainly responsible for sustained emission, while the emission from nanotube originates largely from ends with a characteristic structured ring pattern. I will also present data on the emission stability and uniformity, both of which are essential for successful vacuum microelectronic applications.

2:30 PM U4.3

FIELD EMISSION FROM CARBON NANOTUBE FILMS. Chris Bower, Otto Zhou, University of North Carolina, Chapel Hill, NC; Wei Zhu, Greg P. Kochanski, Sungho Jin, Bell Labs Lucent Technologies, Murray Hill, NJ.

We report on the fabrication and field emission properties of various carbon nanotube films. Nanotubes were processed into randomly oriented films using a variety of techniques. The emission current vs voltage (I-V) characteristics will be presented for both single-walled and multi-walled carbon nanotubes. The I-V characteristics for single-walled carbon nanotubes show deviation from Fowler-Nordheim behavior at high current densities. The maximum stable current density was measured to be in excess of 4A/cm^2 . The emission patterns from carbon nanotubes will be presented.

2:45 PM U4.4

A MICROSCOPIC SCALE INVESTIGATION OF CARBON RELATED MATERIALS BY UHV-SPM. S. Lin, J.B. Xu, J.Z. He, E.Z. Luo, I.H. Wilson, Chinese Univ. of Hong Kong, Dept. of Electronic Engineering, Hong Kong; K.Y. Wang, Univ. of Sci. & Tech. of China, Dept. of Precision Instrumentation, Hefei, PR CHINA.

A modified ultra-high vacuum scanning probe microscope (combination of UHV-AFM, STM, and SFEM) was used to study the local electron field emission properties of carbon related materials. These materials are attractive due to their relatively low turn on field emission property that is highly promising in applications such as cold cathode flat panel display. Tested samples including CVD grown DLC/amorphous carbon thin films, and ion impacted HOPG. Experiments were carried out at pressure lower than 5×10^{-9} torr. Nanoscale topography, apparent local barrier height (LBH) and field emission (FE) current maps were acquired in the same area. Least square fitting show that the localized I-V curves we obtained are more consistent with TAT(Thermal Assisted Tunneling) model rather than F-N (Fowler Nordheim) model.

3:30 PM U4.5

FIELD EMISSION FROM A NEW FORM OF THIN FILM AMORPHOUS CARBON HAVING NANOPARTICLE INCLUSIONS AND NANOTUBES. Gohan Amaratunga, Nalin Rupasinghe, Mark Baxendale, Manish Chhowalla, University of Cambridge, Engineering Dept, Cambridge, UNITED KINGDOM.

Field emission results from a new form of carbon thin film are reported. The films contain carbon nanoparticles (nanotubes, 'onions', 'eggs') within an amorphous carbon matrix and are deposited using a carbon arc with a localized high pressure gas region of He or N_2). The films formed in an N_2 environment have a nitrogenated amorphous carbon (a-C:N) matrix and show clear Fowler-Nordheim type metallic field emission characteristics. The field emission is very similar to that obtained from pure randomly oriented multi and single wall nanotube films. It is proposed that the new a-C:N/nanoparticle films emit electrons through conducting channels formed in the film, sub surface field emission into the a-C:N matrix and hot electrons surmounting of the surface potential barrier between a-C:N and vacuum. Field enhancement factor over 1000 are calculated for the thin film emitters when the nanoparticle work function is taken as 5eV. This class of a-C:N/nanoparticle film holds the potential of being a thin film equivalent to carbon nanotubes in terms of field emission.

3:45 PM U4.6

FIELD EMISSION AND NANOSTRUCTURE OF CARBON FILMS. Vladimir I. Merkulov and Douglas H. Lowndes, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN; Larry R. Baylor, Fusion Energy Division, Oak Ridge National Laboratory, Oak Ridge, TN.

The results of field emission measurements of various forms of carbon films are reported. It is shown that the films' nanostructure is a

crucial factor determining the field emission properties. In particular, smooth, pulsed-laser deposited amorphous carbon films with both high and low sp^3 contents are poor field emitters. This is similar to the results obtained for smooth nanocrystalline, sp^2 -bonded carbon films. In contrast, carbon films prepared by hot-filament chemical vapor deposition (HF-CVD) exhibit very good field emission properties, including low emission turn-on fields, high emission site density, and excellent durability. HF-CVD carbon films were found to be predominantly sp^2 -bonded. However, surface morphology studies show that these films are thoroughly nanostructured, which is believed to be responsible for their promising field emission properties.

4:00 PM U4.7

ELECTRON EMISSION FROM PHASE-PURE NANOCRYSTALLINE DIAMOND THIN FILMS. A.R. Krauss, D.M. Gruen, Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL; O. Auciello, D. Wolf, F. Cleri, Materials Science Division, Argonne National Laboratory, Argonne, IL; M. Ding, Beijing Institute of Electronics, Beijing, CHINA; A. Breskin, R. Chechin, Weizmann Institute, Rehovot, ISRAEL; E. Grossman, Y. Lifshitz, Soreq Nuclear Research Institute, Yavne, Israel; S. Pimenov, V. Konov, A. Karabutov, General Physics Institute, Moscow, RUSSIA; E.I. Givargizov, A. Stepanova, Institute of Crystallography, Moscow, RUSSIA; V. Zhirnov, Semiconductor Research Corporation, Research Triangle Park, NC; A. Rakhimov, N. Suetin, Moscow State University, Moscow, RUSSIA.

Field-induced electron emission from diamond and diamond-like carbon films has been attributed to ion bombardment-induced damaged regions, negative electron affinity, and field-enhancing surface asperities (although the derived values for the effective work function are frequently unrealistic, and the required sharp surface features are usually not observed). Most groups have observed that a mixture of sp^3 and sp^2 binding is required for emission at low threshold fields. We have studied the electron emission properties of well-characterized phase-pure nanocrystalline diamond films. The Fowler-Nordheim analysis yields both an extremely low value of the effective work function and an apparent enhancement of the local electric field that can not be explained in terms of the surface topography. The threshold field for electron emission (as low as 1.5 Volts/ μm) is related to an enhancement in the interband density of states as observed by photoelectron yield measurements vs. photon wavelength. Simple calculations of the interband density of states suggest that the enhancement of state density is associated with quantum well effects at grain boundaries. Pseudopotential calculations based on the observed grain boundary morphology indicate that the grain boundaries consist of a 3.5 Å wide region with sp^2 electronic character, although there is no distinct non-diamond intergranular phase. This model also suggests that the grain boundaries are responsible for both the observed electrical conductivity of the films and the field enhancement factor calculated from the Fowler-Nordheim analysis. STM studies show that electron emission occurs at topographic minima, further suggesting that local field enhancement and electron emission occur at the grain boundaries rather than at topographic asperities. This work was supported by US Department of Energy, BES Material Sciences, under contract W-13-109-ENG-38; Office of Naval Research under contract N00014-97-F-0305.

4:15 PM U4.8

ELECTRON FIELD EMISSION MEASUREMENTS OF A SIMPLE NANOCRYSTALLINE DIAMOND TRIODE. Brock L. Weiss, Andrzej Badzian, Larry Piloni, Materials Research Laboratory, The Pennsylvania State University, University Park, PA.

Field emission characterization has been performed on a simple cold cathode triode device. The cathode material is a thin film nanocrystalline diamond grown by a modified microwave plasma assisted chemical vapor deposition process. The insulating layer is KAPTON film and the extraction gate electrode is a molybdenum mesh. A glass plate, coated with an indium tin oxide, is used as the collector. Field emission characteristics have shown current measurements of greater than 10 microamps for fields of ≈ 20 V/ μm . Gate currents are typically 1000 times greater than the emitted current. Issues currently being addressed include improvement in total emitted current, current stability and device failure. The devices are being evaluated for use in cold cathode ionization gauges for high and ultrahigh vacuum pressure measurements.

4:30 PM U4.9

LOW TEMPERATURE GROWTH OF NANOCRYSTALLINE DIAMOND FILMS ON GLASS SUBSTRATES FOR FIELD EMISSION APPLICATIONS. Timothy D. Corrigan, Argonne National Laboratory, Materials Science and Chemistry Divisions, Argonne, IL, and Northwestern University, Dept of Materials Science and Engineering, Evanston, IL; Alan R. Kraus and Dieter M. Gruen, Argonne National Laboratory, Materials Science and Chemistry Divisions, Argonne, IL; O. Auciello, Argonne National Laboratory,

Materials Science Division, Argonne, IL; R.P.H. Chang, Northwestern University, Dept. of Materials Science and Engineering, Evanston, IL.

Recent studies of field emission from diamond thin films have focused on the investigation of the feasibility of growing diamond films on glass substrates, which are the preferred choice for cost effective flat panel displays. However, diamond growth on glass requires temperatures around 500°C, which is much lower than the temperature needed for growing conventional CVD diamond films. In addition, it is desirable to shorten the deposition time for cost effective processing. We have grown nanocrystalline diamond (NCD) films using a unique microwave plasma technique that involves CH_4 -Ar gas mixtures, as opposed to the conventional CH_4 - H_2 plasma method. The growth species are C_2 dimers, resulting in activation energies of 6 KCal and the ability to grow diamond at lower temperatures than conventional CVD diamond. The NCD films have 2-5 nm grain size, as opposed to the micrometer grains characteristic of conventional diamond films. For the work discussed here, the NCD films were grown with plasma enhanced chemical vapor deposition (PECVD) at low temperatures on glass substrates coated with Ti thin films. The turn-on field was as low as 3 V/ μm for a film grown at 500°C with a gas chemistry of 1% CH_4 /99%Ar at 50 Torr. The films were approximately 250 nm thick with growth times of only one hour. Raman spectroscopy revealed the presence of nanocrystalline diamond in the films. The effect of various growth conditions, including pressure and temperature, on the emission properties of the films will be discussed in terms of their potential application to field emission displays. *Work supported by the U.S. Department of Energy, BES-Materials Sciences under Contract W-31-109-ENG-38, and DARPA/ONR under Contract N00014-97-F-005.

4:45 PM U4.10

ELECTRON EMISSION MECHANISM OF N-DOPED CVD-GROWN DIAMOND COLD CATHODE. Ken Okano, Dept of Physics, International Christian University (ICU), JAPAN; Takatoshi Yamada and Atsuhito Sawabe, Dept of Electrical Engineering & Electronics, Aoyama Gakuin University, JAPAN; Satoshi Koizumi, National Institute for Research in Inorganic Materials, JAPAN; Junji Itoh, Electro-Technical Laboratory, JAPAN.

Recently, the extremely low-threshold electron emission from N-doped diamond cold cathode is reported [1,2], and its electron emission mechanism has attracted much attention [3,4]. In this paper, the voltage drop between the diamond cathode and an anode electrode has been evaluated by changing the anode-cathode spacing. This measurement should provide us with the potential profile between the cathode and the anode, in other words across vacuum. In addition, the electric field in the diamond bulk is evaluated by varying the film thickness. As a result, we have confirmed the strong electric field existing in the diamond bulk and almost no field in the vacuum, as is opposed to the profile often observed in the field emission studies. This strange phenomenon can be explained by the extremely high resistance of N-doped diamond.

[1] K. Okano, S. Koizumi, S.R.P. Silva and G.A.J. Amaratunga, Nature **381**, 140 (1996).

[2] K. Okano, T. Yamada, H. Ishihara, S. Koizumi and J. Itoh, Appl. Phys. Lett. **70**, 2201 (1997).

[3] P. Lerner, N.M. Miskovsky and P.H. Cutler, J. Vac. Sci. and Tech. **B16**, 900-905 (1998).

[4] S.R.P. Silva, G.A.J. Amaratunga and K. Okano, J. Vac. Sci & Tech. **B17**, 557-561 (1998).

SESSION U5: POSTER SESSION: NANOTUBE GROWTH, STRUCTURE, AND PROPERTIES

Chairs: Tatiana Allen and Otto Zhou
Tuesday Evening, November 30, 1999
8:00 P.M.

Exhibition Hall D (H)

U5.1

A SURFACE DIFFUSION MODEL FOR NANOTUBE GROWTH. O.A. Louchev, Y. Sato, National Institute for Research in Inorganic Materials, Tsukuba, JAPAN.

The kinetics of nanotube growth is viewed within the continuous surface diffusion equation [1] coupled with the step-flow model [2]. It is shown that the surface diffusion mechanism provides a growth feeding flux several orders of magnitude higher than that provided by direct collisions into the growth edge from the gas phase, explaining why the nanotube ends remain open during growth. Perturbation analysis shows that surface diffusion, which feeds the growth interface from behind, ensures intrinsic morphological stability of the growing nanotube end. Otherwise, the growth edge would be prone to unstable diffusion limited aggregation and formation of fractal-like structures.

The model shows that the nucleation and subsequent growth of the next layer may inhibit the growth of the underlying layer leading to bamboo structures. It is shown that the presence of a catalyst atom adsorbed on the growth edge is able to decrease surface concentration on the nanotube surface and to inhibit nucleation of the second layer. The effect of possible differences in the activation energies of incorporation into the hexagonal network of adatoms from upper and lower terraces and its implication for layer growth competition are studied. Finally, the formation of BCN nanotubes with well separated layers of C and BN [3] is discussed. The authors of [4] propose that these nanotubes grow from a liquid drop through a unidirectional eutectic growth mechanism. We propose an alternative model within which the layer separation is caused by a phase segregation mechanism at the growth edges in surface diffusion step-flow layer growth. [1] O.A. Louchev, Appl. Phys. Lett. 71 (1997) 3552; [2] O.A. Louchev and Y. Sato, Appl. Phys. Lett. 74 (1999) 194. [3] K. Suenaga et al., Science 278 (1997) 653. [4] K. Suenaga et al., Applied Physics A 68 (1999) 301.

U5.2
STRUCTURE AND PROPERTIES OF ALIGNED, MULTIWALL, CARBON NANOTUBES. A.M. Rao, D. Jacques, S. Villain, R.C. Haddon, Center for Applied Energy Research, University of Kentucky Lexington, KY; W. Zhu, S. Jin, Bell Laboratories, Lucent Technologies Murray Hill, NJ.

Aligned arrays of multi-walled carbon nanotubes (MWNTs) were synthesized from the catalytic decomposition of a ferrocene-xylene mixture using a quartz tube reactor at 700 degrees C. Unlike other methods used for the growth of aligned nanotubes, our process does not use preformed substrates or the deposition of catalyst metal layers such as Ni or Co. Transmission electron microscope (TEM) and scanning electron microscope (SEM) images of individual MWNTs show that the average tube diameter is ~ 20 nm and the tube length is ~ 2-10 microns, controllable with processing parameters. The effect of various metallic, oxide or compound substrates on nanotube nucleation and growth kinetics in our CVD techniques has been investigated. It is shown that the MWNT diameter and density can be significantly altered by the nature of the substrate chosen. It is also interesting to note that most metallic substrates are not favorable to the nucleation of nanotubes in our ferrocene-xylene system. We have evaluated the properties of our aligned MWNTs, including field emission properties. Excellent field emission was observed at low operating field values (2-3 volts /micron) with current densities of at least 50 mA/cm².

U5.3
ALIGNED CARBON NANOTUBES GROWN ON SILICON VIA MICROWAVE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION. Hongtao Cui¹, Otto Zhou^{1,2} and Brian R. Stoner^{1,2};
¹Univ. of North Carolina, Curriculum in Applied and Materials Sciences, Chapel Hill, NC, ²Univ. of North Carolina, Dept. of Physics and Astronomy, Chapel Hill, NC.

Aligned multi-wall carbon nanotubes were deposited on silicon by microwave plasma enhanced chemical vapor deposition using methane/ammonia mixtures. Substrates were oxidized and then seeded with a thin film of metal catalyst prior to deposition. The methane-to-ammonia ratio, total pressure, substrate temperature, microwave power, and catalyst material were varied to affect both the nucleation and growth of the carbon nanotubes. The morphology, structure, and alignment were studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and x-ray diffraction (XRD). SEM analysis reveals a densely packed, highly uniform array of carbon nanotubes. Polar XRD confirms that the tubes are strongly aligned with the tube axis perpendicular to the surface. Initial data show that the alignment is strongly dependent upon both substrate temperature and partial pressure of carbon in the gas phase. TEM data show that both concentric and bamboo-type multi-wall structures with diameters ranging from 30-90 nm were formed, dependent upon process conditions. High quality, smaller diameter tubes appear to grow at lower temperatures, however further experiments and data analysis must be conducted in order to confirm this trend. The microwave system employed operates at a center frequency of 915 MHz, has a maximum power capability of 10kw and allows for independent control of substrate heating through a resistively heated graphite heater.

U5.4
CATALYTIC GROWTH OF CARBON NANOTUBES ON THE SURFACE OF SiC. Balvinder Gogia, A. Gotoh, Joint Research Consortium of FCT, Japan Fine Ceramic Center, c/o National Institute of Materials and Chemical Research, Tsukuba, JAPAN; M. Kusunoki, Japan Fine Ceramic Center, Nagoya, JAPAN; T. Nakamura, Y. Koga, National Institute of Materials and Chemical Research, Tsukuba, JAPAN.

Carbon nanotubes are the focus of intense interest recently owing to their promising physical properties. These nanotubes could give impact to various areas of technological applications from superstrong composites to nanoelectronics. In order to achieve these goals, there is a need to have a simple and reproducible synthesis method to yield a uniform distribution of nanotubes over a large area. In this paper, we report the synthesis of carbon nanotubes on the surface of doped and undoped SiC when exposed to Nd-YAG laser (532 and 1064 nm) and/or annealed in furnace under various atmospheric conditions including N₂, Ar, air, vacuum, etc. The different varieties of commercially available α - and β -SiC powders were investigated for the purpose. The samples had been characterized by various techniques including SEM, EPMA, TEM etc. The morphology of features, observed on the surface of SiC, varied from long rod like to fine thread like depending upon whether the annealing was done under vacuum or gas atmospheric conditions. These fine thread like features are nothing but carbon nanotubes (bundled together) as per compositional analysis by EPMA. Doping of SiC with various catalysts (Ni, Co, Pt) not only increased the growth rate of the carbon nanotubes on the surface of SiC but also their density and size. The typical size was 20-50 nm in diameter and about 1 μ m in length when synthesized in N₂ gas atmosphere (100 Torr). Further, the effect of various other parameters including the laser beam intensity, exposure time, initial particle size on the growth and physical properties of these nanotubes will also be highlighted.

U5.5
CVD GROWTH OF NANOTUBES ON NANOPARTICLE CATALYSTS. John M. Nugent, Amanda Giermann, R.W. Siegel, P.M. Ajayan Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY.

Several types of metal and metal oxide nanoparticles were used as catalysts to grow carbon nanotubes by rapid and conventional chemical vapor deposition (CVD). The morphology and structure of the nanotubes grown under different CVD conditions and on different catalysts will be reported. The catalysts used range from Pd nanoparticles to nanophase iron oxide. The effects of nanoparticle catalyst size on nanotube growth will be discussed. The growth of novel carbon structures during rapid thermal CVD conditions will also be described.

U5.6
STRUCTURAL TAILORING OF GRAPHITE NANOFIBERS THROUGH UTILIZATION OF SPECIFIC SUPPORT MATERIALS. Paul E. Anderson and Nelly M. Rodriguez, Department of Chemistry, Northeastern University, Boston, MA.

The decomposition of hydrocarbons over selected metal catalysts is becoming a major route of production of carbon nanostructures, namely the graphite nanofiber (GNF). The materials show tremendous potential as hydrogen storage devices, field emitters, catalyst supports, and nanocomposite reinforcements. Each specific application requires one to accurately manipulate the morphology, conformation, and orientation of the graphite layers, which are all controlled by catalyst and feed gas composition, temperature, and other variables. Although unsupported metal catalysts tend to yield larger GNF structures, true nano-dimension fibers are obtained by supported catalyst systems, which disperse the metal into consistent small particles. Although the support material has long been regarded as an inert substrate, it is now known it exerts a significant influence on the metal particle through a combination of electronic and geometric effects. In almost all cases, the supported fibers are completely different than their larger unsupported counterparts. A number of transition metal and bimetallic catalysts on various supports (silica, SP1 Graphite, GNF) and their resulting structures will be reviewed. Techniques used to characterize the GNFs include high resolution transmission electron microscopy, electron diffraction, and temperature programmed oxidation. In almost all cases, the nanofiber characteristics can be explained by traditional metal/support interaction theory, catalytic gasification of graphite experimental data, and solid state chemistry.

U5.7
SINGLE CRYSTAL GRAPHITE PLATES GROWN IN MPACVD WITH Ni ASSISTANCE. Teresa Badzian, Andrzej Badzian, Rustum Roy, The Pennsylvania State University, Materials Research Laboratory, University Park, PA; Shang-Cong Cheng, The Pennsylvania State University, Materials Characterization Laboratory, University Park, PA.

While fullerenes and nanotubes have attracted a lot of attention because of the new atomic bonding networks and exceptional properties the question of why graphite does not grow in the form of extensive flat plates remains unanswered. Growth from the gas phase of extensive flat plates (over one micrometer in linear dimension) of graphite is a rare phenomenon. We report here on a microwave plasma

process which allows one to grow graphite plates over 100 micrometers long and five micrometers wide. The process is based on etching both graphite and nickel simultaneously via hydrogen plasma. The chemical composition and the Raman signature (1580 reciprocal centimeters) of graphite have been confirmed. Traces of Ni have been detected by electron microprobe on graphite and on diamond crystals. No agglomerations of Ni have been found. Simultaneous growth of diamond and graphite is a common phenomenon for a variety of CVD processes. Isometric diamond crystals and graphite plates were formed simultaneously. The morphology of graphite plates indicates a single crystal nature because the edges fit a hexagonal symmetry. Diamond crystals nucleate at the edges as well as on both sides of the graphite plate. Secondary electron images show diamond crystals on the top surface of the graphite and somewhat blurred images of diamond crystals nucleated on the backside of the plate. This means that the graphite plate is ultrathin and secondary electrons ejected from the diamond surface penetrate the plate of graphite on their way to the SEM detector. TEM study confirms the single crystal nature of graphite plates. Electron diffraction indicates the $\langle 1 \text{ minus } 100 \rangle$ direction as fastest growth.

U5.8

CONTROLLED GROWTH OF INDIVIDUAL MULTIWALL CARBON NANOTUBES. Z.P. Huang, D.Z. Wang, J.G. Wen, Z.F.

Ren, Department of Physics, Boston College, Boston, MA; J.H. Wang, Department of Chemistry, SUNY at Buffalo, Buffalo, NY; L.E. Calvet, J. Chen, J.F. Klemic, M.A. Reed, Department of Electrical Engineering, Yale University.

Controlled growth of individual multiwall carbon nanotubes on submicron nickel dots on silicon have been achieved by plasma enhanced hot filament chemical vapor deposition (PEHFCVD) below 660°C. A nickel dot (100 nm thickness and diameter) array was fabricated by standard electron beam photolithographic techniques. PEHFCVD was done using acetylene (C_2H_2) gas as the carbon source and ammonia (NH_3) as a catalyst and dilution gas. 1, 2 and 5 μm spacing well-separated single carbon nanotubes were observed. The single nanotubes had rounded base diameter of approximately 150 nm, heights ranging from 0.1 to 5 μm and sharp tips with a less than 10 nm average radius. The height changed with the growth time. This nanotube growth process is compatible with integrated circuit processing. Therefore, it is an extremely promising method to fabricate field emission device, sensor and scanning probe microscopy.

U5.9

DIAMETER CONTROL IN THE FORMATION OF SINGLE-WALL CARBON NANOTUBES. Rahul Sen, Yohsuke Ohtsuka, Toshinobu Ishigaki, Daisuke Kasuya, Shinzo Suzuki and Yohji Achiba, Dept of Chemistry, Tokyo Metropolitan University, Tokyo, JAPAN; Hiromichi Kataura, Dept of Physics, Tokyo Metropolitan University, Tokyo, JAPAN.

Growth of single-wall carbon nanotubes (SWNTs) by the laser evaporation of metal catalyzed graphite targets in argon gas has attracted lot of attention in recent years. This technique provides precise control over various experimental parameters such as temperature, pressure, gas flow rate and laser power. Effect of pressure on the yield and growth temperature on the diameter of the distribution of SWNTs has been reported. In this work we have systematically varied the position of the target with respect to the hot zone of the furnace and studied the effect of target position on the diameter distribution and yield of SWNTs. We have also investigated the effect of gas flow rate on the diameter distribution of SWNTs. The samples were examined by Raman spectroscopy and Transmission Electron Microscopy.

U5.10

SYNTHESIS, MODIFICATION AND ELECTRONIC PROPERTIES OF MULTIWALL CARBON NANOTUBES PRODUCED IN ARC-DISCHARGE. A.V. Okotrub, Yu.V. Shevtsov, A.V. Gusel'nikov, I.S. Fedorov, N.F. Yudanov, Yu.V. Shubin, I.P. Asanov, A.I. Romanenko, L.G. Bulusheva, Institute of Inorganic Chemistry SB RAS, Novosibirsk, RUSSIA; A.L. Chuvilin, N.A. Rudina, Boreksov Institute of Catalysis SB RAS, Novosibirsk, RUSSIA.

Carbon nanotubes were produced using a set-up of arc-discharge evaporation of graphite. The influence of gas pressure in the vacuum-chamber of set-up on the yield of multiwall carbon nanotubes was studied. High-resolution transparent microscopy was used to determine the shape and morphology of carbon nanoparticles in an inner part of deposit growing on the cathode. At the pressure of 1.3 atm the inner part was shown to consist of 90 percents of multiwall carbon nanotubes. From scanning electron microscopy measurement the nanotubes have predominant orientation in the plane perpendicular to the deposit growth axis. Number of concentric shells in the separate nanotube and their chirality were determined. The influence of the impurities (d and f - metals) on the morphology of

carbon nanoparticles was investigated also. Fluorination and bromination of samples of multiwall carbon nanotubes were performed at the room temperature. Chemical composition of the modified carbon nanotubes was determined with photoelectron spectroscopy. Electrical resistivity of the samples with different content of the nanotubes was measured with four-contact method in temperature interval from 4 to 400 K. Conductivity some increases with the decreasing temperature, indicating the samples as a disordered conductor with localized electrons. The resistivity measured at ambient conditions along textured samples is higher roughly 30 times that measured in the normal direction.

U5.11

CUTTING SINGLE WALLED CARBON NANOTUBES.

Ingrid Stepanek, Université Montpellier II, Montpellier, FRANCE and CCR Ispra, EI, Ispra, ITALY; Guillaume Maurin, Université MontpellierII, LPMC, Montpellier, FRANCE; Julie Gavillet, LEM, ONERA, Chatillon, FRANCE; Patrick Bernier, Université Montpellier II, Montpellier, FRANCE.

Single walled carbon nanotubes are potentially good adsorbents if they can be open easily. We investigated a mechanical cutting technique with small diamond particles (nanometer scale). This technique is supposed to preserve the bundle structure while acid treatments degrade a large part of the outer surface of the ropes. The obtained sample was characterized by SEM, HRTEM, nitrogen adsorption, Raman spectroscopy and X ray diffraction. The efficiency of the method will be discussed.

U5.12

PURIFICATION AND CHARACTERIZATION OF SINGLE-WALL CARBON NANOTUBE. H.Y. Kim, W.B. Choi, D.S. Chung, J.H. Kang, I.T. Han, J.M. Kim, Samsung Advanced Institute of Technology, Suwon, KOREA; M.H. Moon, Kangnung Univ, Dept of Chemistry, Kangnung, KOREA.

Single-wall carbon nanotubes (SWNTs) have recently been considered as a new class of electronic materials because of their ultra narrow tube diameters and unique electrical properties, which are strongly dependent on their diameter and chirality. These SWNTs are easily produced by arc discharge method which results in extremely long, highly tangled nanotubes. Also, they contain large amounts of impurities such as amorphous carbon and catalytic metal particles. Therefore, the development of suitable method for purification and separation of nanotubes is crucial for further progress on nanotubes. In this study, SWNTs were purified and cut into short length by the liquid phase oxidation using typical oxidants such as HNO_3 , H_2SO_4 and their mixtures of various volume ratio. The SWNT-acid solution is refluxed at high temperature, filtered with poly tetra-fluoro ethylene filtering paper, rinsed with distilled water, and then dried at room temperature. In order to find the optimum purifying condition with little damage on SWNT surfaces, reaction conditions (temperature, reflux time, and etc.) were changed. Through this method, purified SWNTs with the length of less than 1 μm were successfully obtained, which was confirmed by scanning electron microscopy and tunneling electron microscopy. The purified SWNTs were analyzed further by Raman scattering and, powder X-ray diffraction. Moreover, field emission characteristics of purified SWNTs were analyzed to study the effect of purification on the field emission. It was found that the uniformity of field emission was enhanced after purification.

U5.13

SOLUBLE-, INSOLUBLE-FULLERENES AND CARBON NANOSPHERE. Yohji Achiba, Toshinobu Ishigaki, Yohsuke Ohtsuka, Shinzo Suzuki, Tokyo Metropolitan Univ, Dept of Chemistry, Tokyo, JAPAN; Hiromichi Kataura, Tokyo Metropolitan Univ, Dept of Physics, Tokyo, JAPAN.

The formation and structures of several different kinds of carbon nanoparticles such as solvent soluble fullerenes, insoluble fullerenes and carbon nanosphere with sizes around 1.0 nm will be presented and discussed on the basis of several kinds of spectroscopic observations such as mass spectroscopy, transmission electron microscopy and Raman scattering spectroscopy. Laser ablation of graphite in the rare gas atmosphere gives rise to the formation of various kinds of carbon nanoparticles. The yield of each species were found to be much dependent on the condition such as ambient temperature and pressure. Raman spectroscopy was applied to identify these species from the view points whether these species possess fullerene cage structure or not. As a result, it was found that both the soluble and insoluble fullerenes give a clear evidence of the presence of fullerene cages in their Raman spectra, whereas the carbon nanosphere with sizes around 1.0 nm does not show it.

U5.14

ISOMERIC HIGHER AND SMALLER FULLERENES: A PROFOUND ENTHALPY/ENTROPY INTERPLAY. Xiang Zhao,

Zdeněk Slanina, Eiji Ōsawa, Laboratories of Computational Chemistry & Fullerene Science, Department of Knowledge-Based Information Engineering, Toyohashi University of Technology, Toyohashi, JAPAN.

Early results from the eighties for small carbon clusters like C_4 or C_6 have suggested that the combined quantum-chemical and statistical-mechanical computations could show some interesting temperature effects also for isomeric fullerenes. This feature was first demonstrated on some C_{50} isomers. The fullerene research has indeed supplied several sets of isomeric higher fullerenes. At present over twenty stable fullerenes C_n have been identified with n varying from 60 to 96. Several such mixtures of fullerene isomers have been computed (C_{76} till C_{94}) and an agreement with observations found. Hence, the computations have demonstrated that the presumption of partial, inter-isomeric thermodynamic equilibrium is actually well working. One of the biggest systems computed within the partial thermodynamic-equilibrium treatment so far is C_{92} with 86 IPR isomers. The reported computations are based on semiempirical (SAM1), *ab initio* SCF (HF/4-31G), and DFT (B3LYP/6-31G*) approaches and RRHO partition functions. The entropy considerations also indicate an interesting way for non-IPR structures stabilization, illustrated on C_{72} and C_{74} . The approach is also applied to smaller fullerenes like C_{36} . As fullerenes are formed at high temperatures, entropy effects should be important owing to the temperature enhancement. It turns out for C_{36} that in the most sophisticated computational approximation used, B3LYP/6-31G*, just two structures are controlling the region of higher temperatures: the conventional fullerenes D_{6h} and D_{2d} . Although the D_{2d} ground state has to prevail at low temperatures, the stability order is reversed by entropy effects already at a temperature of 1500 K.

U5.15

AB-INITIO MOLECULAR DYNAMICS SIMULATION OF LASER-INDUCED TRANSFORMATIONS OF FULLERITE.

Alfredo Gambirasio, Marco Bernasconi, Giorgio Benedek, INFN and Dept of Materials Science, Milano-Bicocca Univ, Milano, ITALY; Pier Luigi Silvestrelli, Dept of Physics, Padova Univ, Padova, ITALY; Michele Parrinello, Max-Planck Inst FKF, Stuttgart, GERMANY.

We present the results of a theoretical study of the transformation of fullerite induced by very short (≈ 100 fs) laser pulses. We have performed *ab-initio* molecular dynamics (MD) simulations based on finite temperature density functional theory [P. L. Silvestrelli *et al*, *Phys. Rev. Lett.* **77**, 3149 (1996)]. It is known experimentally that fullerite undergoes different transformations upon laser irradiation such as polymerization, coalescence and cage-opening, depending on chemical environment and on irradiation conditions (fluence, wavelength and duration of the laser pulses). Thermal and electronic effects are responsible of these transformations, but further investigation is needed to clarify their interplay. Previous experimental and theoretical studies on laser melting of semiconductors (Si and GaAs) and graphite have shown that, under irradiation with very short laser pulses, melting is not driven by heating of the ions via electron-lattice energy transfer but occurs because of the modification of the bonding properties induced by the high level of electronic excitation (non-thermal melting). We performed *ab-initio* MD simulation at different electronic temperature (T_{el}). We find that for electronic excitation corresponding to $T_{el} \leq 30000$ K, the C_{60} cages do not break but undergo wide breathing deformation, while at 40000 K the C_{60} cages break in about 50 fs and a fluid phase is formed. The ionic temperature of the hot-electrons fluid is 2500 K, much lower than the melting temperature of carbon at normal conditions (≈ 4500 K). The structural properties are very different from those of ordinary liquid carbon. We predict that the differences in the optical conductivity between the hot-electrons fluid and crystalline fullerite might allow to identify the non-thermal melting process by time-resolved spectroscopy. We estimate the threshold fluence for the non-thermal cage-opening to be ~ 480 mJ/cm².

U5.16

LANGMUIR-BLOGETT FILM OF THE ENDOHEDRAL METALLOFULLERENE Dy@C82.

Houjin Huang, Shihe Yang, Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, HONG KONG.

Multilayer Langmuir-Blgett film of the endohedral metallofullerene Dy@C82 was constructed at the air-water interface. Patterned structures (ordered, ringed etc.) were clearly observed by high resolution TEM, indicating that the metallofullerene can survive at the air-water interface. Electron diffraction pattern shows that the metallofullerene cages have preferred orientation in the constructed film. Blue-shifted UV-Vis absorption peaks were found and attributed to the strong interaction among the metallofullerene particles, which can be correlated to the enhanced stability of the metallofullerene due to the changed electronic structure. X-ray photoelectron spectra show that the carbon cages were partially oxidized, which can be reduced when the film was prepared under inert environment.

U5.17

DIRECT OBSERVATION OF INTERCALANT AND CATALYST PARTICLE IN SINGLE WALL CARBON NANOTUBES.

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Two fundamentally important structure-property relationships are to be established in carbon nanotubes. One is the sizes and distributions of catalyst metal particles which would directly relate to the growth mechanism. The other is the site and distribution of dopant atoms which may lead to an interpretation of property enhancements upon intercalation. Little has been done in both these areas due to the difficulties of directly observing dopant atoms and nano-particles using conventional phase contrast electron microscopy. However, by using the Z-contrast imaging technique, the scattered intensity is a function of atomic number, Z^2 , so that heavier atoms can be resolved directly even at atomic level. In this study, we use a VG Microscopes HB603U STEM to investigate both the distribution of metal catalyst particle in the laser ablation grown, and the distribution of iodine dopant atoms arc-grown SWNT. The Z-contrast STEM image reveals that the iodine is incorporated within some particular nanotubes but is not seen in others in the same bundle. Higher resolution Z-contrast images, two chains of iodine atoms are visible. The maximum separation of the two strands is about 0.65nm, much less than the diameter of the SWNT. It is clear that the iodine atomic chains are inside each SWNT, and the changing spacing of the two strands suggests that the chains spiral along the walls in the form of a double helix. This configuration is confirmed by the first-principles total energy calculations. Using the same method, we also observe the metal catalyst particle distribution within the nanotube bundles made by the pulse laser ablation. The particle size is generally less than 20nm, but the Z-contrast image also clearly reveals particles as small as 1-2nm, not seen in bright field phase contrast image, providing new insights into the growth mechanism.

U5.18

DYNAMICS IN LITHIUM FULLERIDES FROM QUASIELASTIC AND INELASTIC NEUTRON SCATTERING.

L. Cristofolini, M.P. Fontana Dipartimento di Fisica and INFN, Universita' di Parma, ITALY; G. Cicognani, A.J.Dianoux INFN and ILL, Grenoble, FRANCE.

Following our success in synthesizing and characterizing a pure phase highly doped lithium fulleride $Li_{12}C_{60}$ consisting of Li clusters intercalated within the pristine fullerene structure, we present here more recent results on the dynamics of the Li^+ ions and of the C_{60} molecular units in $Li_{12}C_{60}$ obtained by INS and QENS experiments performed on IN6 (ILL) covering the temperature range from 150K to 600K. We will show that the transition from the high temperature $Fm\bar{3}m$ to the low temperature tetragonal structure is accompanied by significant changes in the fullerene part of the vibrational DOS. A further insight into the role of the Li^+ vibrational and diffusional motion is derived from a detailed analysis of the T and Q dependence of the width and of the intensity of the incoherent QENS. We will discuss different models of Li motion, i.e. localized within a single void of the fullerene structure and delocalized between different voids.

U5.19

LOCAL STRUCTURE OF NANOPHASE AMORPHOUS SP² CARBONS: GRAPHENE FLAKES AND NANOPORES.

John Fischer, Agnes Claye, University of Pennsylvania, Dept. of Materials Science and Engineering, Philadelphia PA.

Hard (non-graphitizable) carbons, with primarily sp^2 bonding, exhibit substantially higher Li capacities than graphite and can be made from cheap precursors. Thus they are very attractive to Li ion battery manufacturers, however little is known about the microscopic mechanism(s) of reversible Li bonding. Here we describe two applications of neutron scattering to address the lack of fundamental understanding of these materials. Elastic scattering and radial distribution function analysis allows to determine the local structure, and to study how it evolves with processing. Small-angle scattering reveals monodisperse pores *ca.* 1 nm in diameter, which are shown not to be important contributors to the high Li capacity.

U5.20

THEORETICAL STUDIES OF LITHIUM INTERCALATION INTO CARBON NANOTUBES.

R.L. Jaffe, NASA Ames Research Center, Moffett Field, CA; J. Han, MRJ Technology Solutions, NASA Ames Research Center, Moffett Field, CA.

Lithium intercalation into graphite has been subject to considerable study. In Li-ion batteries, the loading of lithium between graphite layers results in a Li/C ratio of 1/6 and an increase in the normal interlayer spacing of graphite from 3.4 to 3.9 Å. Initial results using carbon nanotubes instead of graphite indicate higher loadings are possible. We have utilized ab initio quantum chemistry calculations to study the interaction of Li neutrals and cations with model polycyclic aromatic molecules representing planar graphene sheets and curved carbon nanotubes. Our goal is to determine differences in the metal-carbon interaction that could account for the observed higher Li loading in nanotubes. In addition, we study the interaction of Li ions with carboxyl and hydroxyl groups that are known to form on the open ends of nanotubes. Strong binding between the lithium and oxygen can serve to prevent the metal from intercalating into or around the open tubes. It is also a possibility.

U5.21

ALKALI-METAL CONTAINING AMORPHOUS CARBON: REACTIVITY AND ELECTRONIC STRUCTURE. Matthias Toewe, Petra Reinke, Peter Oelhafen, Institut fuer Physik der Universitat Basel, Basel, SWITZERLAND.

Applications in energy research (e.g. fusion devices, electrodes in lithium batteries) have stimulated interest in the interaction of alkali metals with carbon and in the reactivity of the combination of these materials. In this work we prepared amorphous hydrogen-free carbon films (sp^2 -dominated a-C) which served as matrices for the incorporation of lithium and sodium, respectively. Experiments were carried out in an ultrahigh-vacuum (UHV) apparatus which allows in-situ sample characterization by photoelectron spectroscopy with both x-ray and ultraviolet excitation (XPS, UPS) and by electron energy loss spectroscopy (EELS). Initially, metal content in the surface region did not exceed about 10at%. Metal core level spectra revealed variations in metal bonding depending on the structure of the carbon matrices. This led to the development of a simple model for the incorporation of metal atoms and for the reaction paths within the material. The reactivity of the samples was tested by exposure to molecular oxygen and atomic hydrogen before or after metal incorporation. Annealing up to 1100°C concluded the experimental series. Upon oxygen exposure the metal is oxidized and a reaction driven accumulation of metal atoms to up to 50 at% mainly in oxidic form takes place at the sample surface. The sample's work function is strongly reduced by this process and can become less than 2eV. Even after storage in air for several months work functions remain low although chemical changes occur in the sample surface. The influence of atomic hydrogen on the accommodation of metal atoms was investigated. Effects of treatment with thermal hydrogen atoms are small, but in agreement with our incorporation model.

U5.22

HYDROGEN STORAGE CAPACITY OF CARBON NANOTUBES. Seung Mi Lee, Jin Moon Bok, Dept. of Semiconductor Science and Technology and Semiconductor Physics Research Center, Chonbuk Nat'l Univ., Chonju, SOUTH KOREA; Thomas Frauenheim, Universitat-GH Paderborn, Fachbereich Physik, Thoretische Physik, Paderborn, GERMANY; Marcus Elstner, Dept. of Physics, Harvard Univ., Cambridge, MA; Yong Gyo Hwang, Department of Physics, Wonkwang University, Iksan, SOUTH KOREA; Young Hee Lee, Dept. of Physics, Dept. of Semiconductor Science and Technology and Semiconductor Physics Research Center, Chonbuk Nat'l Univ., SOUTH KOREA.

Hydrogen storage capacity of single- and multi-walled carbon nanotubes was investigated using density-functional tight-binding calculations. Large quantity of hydrogen atoms can be stored as a form of H_2 molecules in large empty space of single-walled carbon nanotubes. We predict that the charge storage capacity reaches 2200 mAh/g for (5,5) tube and this value increases linearly with the diameter of nanotubes. Experimentally well observed (10,10) nanotubes can store charges as large as 4400 mAh/g. In case of multiwalled nanotubes, hydrogen atoms favor either to adsorb on outer top sites of graphitic shells or to form H_2 molecules between shells, giving smaller values of storage capacity of about 1500 mAh/g, independent of the diameter. These values are much larger than that of the conventional metal hydrides. Molecular dynamics simulations further show that single-walled nanotubes can store hydrogen atoms kinetically more easily than multiwall nanotubes. We conclude that single walled carbon nanotubes are more efficient than multi-walled carbon nanotubes for hydrogen storage vehicle.

U5.23

ELECTROCHEMISTRY OF CARBON NANOTUBES. Jinhua Chen, Zhongping Huang, D.Z. Wang, Zhifeng Ren, Boston College, Dept of Physics, Chestnut Hill, MA; J.H. Wang, State University of New York at Buffalo, Dept of Chemistry, Buffalo, NY.

The electrochemical behavior of large arrays of well-aligned carbon

nanotubes has been investigated by cyclic voltammetry in aqueous and non-aqueous electrolytic solutions. The effects of growth conditions and pretreatment on the electrochemical behavior of these carbon nanotubes have also been discussed.

U5.24

PREDICTIONS OF STRUCTURAL AND ELECTRONIC PROPERTIES OF FLUORINATED SINGLE WALL CARBON NANOTUBES BY QUANTUM CHEMISTRY AND TIGHT BINDING CALCULATIONS. L. Yang, ELORET, Inc., Sunnyvale, CA; R.L. Jaffe, NASA Ames Research Center, Moffett Field, CA; M.R. Anantram, MRJ Technology Solutions, NASA Ames Research Center, Moffett Field, CA.

Recently Mickelson and coworkers reported the fluorination of the sidewalls of single wall carbon nanotubes (Chem. Phys. Letters, 1998, 296, 188) in a manner similar to that used previously for graphite and fullerenes. We have utilized ab initio quantum chemistry calculations (using hybrid density functional theory, DFT) to study the energetics of possible fluorination reaction products. When fluorine adds to a fullerene or nanotube, it transforms the underlying carbon atom to sp^3 hybridization and introduces a localized change in geometry. We use the well-established fluorination chemistry of fullerenes to calibrate these calculations ($C_{60}F_{18}$ and $C_{60}F_{36}$ are the products with greatest yield). The electronic properties of selected fluorinated nanotubes are calculated using a 4-orbital tight binding hamiltonian. We study the effect of number and arrangement of attached fluorine atoms on the electronic structure (band gap, electron density) and conductivity of the nanotubes.

U5.25

ELECTRONIC INTERACTION BETWEEN SINGLE-WALL CARBON NANOTUBE BUNDLES. N. Snider, S. Paulson, University of North Carolina at Chapel Hill, Dept of Physics and Astronomy, Chapel Hill, NC; A. Seeger, A. Helser, S. Razzaque, R.M. Taylor III, University of North Carolina at Chapel Hill, Dept of Computer Science, Chapel Hill, NC; R. Superfine, S. Washburn, University of North Carolina at Chapel Hill, Dept of Physics and Astronomy, Chapel Hill, NC.

A nanoelectronic device has been created consisting of two parallel single-wall nanotube bundles with 4-probe metallic contacts to each. This device was created with a newly developed technique which allows the direct manipulation of the bundles into an arbitrary configuration with an advanced interface to an AFM, and placement of registered metal contacts by a combination of photolithography and electron beam lithography. Preliminary electronic measurements of the inter-bundle nanotube-nanotube interaction will be reported. This work is supported by the following grants: NSF-ECS-9700677, NSF-ASC-9527192, ONR-N0014-98-1-0597

U5.26

STUDY OF CARBON NANOTUBES UNDER HIGH PRESSURE. Jie Tang¹, A. Matsushita¹, S. Bandow², M. Yudasaka³, L.C. Qin³, S. Iijima^{2,3}, ¹National Research Institute for Metals, Tsukuba, JAPAN; ²JST-ICORP Nanotubulite Project, Nagoya, JAPAN; ³JST-ICORP Nanotubulite Project, Tsukuba, JAPAN.

Single-walled carbon nanotubes have much lower mass density than other forms of solid carbon materials such as graphite, diamond, or the various fullerenes. Raft-like bundles of single-walled carbon nanotubes of various lengths, produced by laser evaporation of graphite catalyzed by Ni / Fe nano-particles, have been studied under high pressure with in situ synchrotron / X-ray diffraction and other analytical techniques. The inter-tubular distances in the nanotube bundles have been measured as a function of the applied pressure and they have been correlated with the structural changes that the nanotubes have under gone under high pressure. In particular, when the carbon nanotubes are subject to high pressure, the circular cross-section tend to polygonize and this would effectively shorten the inter-tubular distances. Results on the measurement of transport properties such as the electrical conductivity and the thermal conductivity of single-walled carbon nanotubes under high pressure will also be presented and discussed.

U5.27

THERMOELECTRIC POWER OF ALIGNED AND RANDOMLY ORIENTED CARBON NANOTUBES. Mark Baxendale, Guan Lim, Gehan Amarantunga, Cambridge University, Engineering Department, Trumpington St, Cambridge, UNITED KINGDOM.

Thermoelectric power (TEP) was used to elucidate the electrical transport properties of aligned and randomly oriented carbon nanotube systems in the temperature range 77 K - 450 K. A weakly negative TEP, comparable with that of a graphite flake, was observed for a macroscopic bundle of multiwall carbon nanotubes (MWNTs) with individual axes aligned parallel to the main axis. However, mats

of randomly oriented MWNTs gave a strongly positive TEP, as did mats of single-wall nanotubes (SWNTs). Compressed SWNT mats have an intermediate weakly positive TEP. This is evidence of the importance of inter-tube contacts in the interpretation of the TEP data for carbon nanotube systems. Models for TEP behaviour incorporating contact effects are described and used to interpret the non-Ohmic low-temperature conductivity regime.

U5.28

ELECTRON SPIN RESONANCE AND STATIC MAGNETIC SUSCEPTIBILITY OF SINGLE-WALL CARBON NANOHORN PARTICLES. Shunji Bandow, ^aICORP-JST, Meijo Univ. Dept.

Physics, Tenpaku, Nagoya; Masako Yudasaka, ^bICORP-JST, NEC Fundamental Research Lab. Miyukigaoka, Tsukuba; Fumio Kokai, Kunimitsu Takahashi, Institute of Res. & Innov., Kashiwa, Chiba; Sumio Iijima, ^{a,b}.

The single-wall carbon nanohorns (SWNHs) are produced by a CO₂ laser vaporization of a carbon target in an Ar gas. The structural feature of SWNH is illustrated by rolling up a graphene sheet to form a cylinder with a typical diameter of ≈ 2 nm and a length of 20 - 30 nm, and by terminating in the edge region by reducing the tube diameter like the corn with a corn angle of 20 degrees. To explain the angle of 20 degrees, it is necessary to put 5 pentagons at the tip region of the SWNH. The pristine SWNHs were ESR active and the linewidth ΔH was susceptible to the pressure of O₂ gas. However, the integrated intensity of the ESR signal did not depend on the O₂ pressure, suggesting an intrinsic ESR signal associated with a characteristic spin state of SWNH. The spin concentration was estimated at the order of 10^{18} emu/g, which corresponds to 1 spin per 10 - 100 SWNHs. Measurement of the magnetization curve for pristine SWNHs was carried out at the temperatures of 4.2 and 300 K with the magnetic field up to 7 T. The magnetization curve can be analyzed by a superposition of the Aharonov Bohm effect and the spin paramagnetism with a spin quantum number of 3/2.

U5.29

PHONON-ASSISTED OPTICAL EXCITATION IN CARBON NANOTUBES. Ping Chen, Jianyi Lin, Kuan Lee Tan, National Univ, Dept of Physics, SINGAPORE.

Phonon-assisted optical excitation has been observed on carbon nanotubes made in our lab. The diameters of the nanotubes are estimated from high resolution transmission electron microscope. A 0.1 eV band gap is determined for the semiconducting multi-walled carbon nanotubes, in a very good agreement with the theoretical prediction. This is the first example that the band gap of carbon nanotubes can be directly measured by optical spectroscopy.

U5.30

RESONANCE RAMAN SCATTERING OF MULTI-WALLED CARBON NANOTUBES. Hiromichi Kataura, Tokyo Metropolitan Univ, Dept of Physics, Tokyo, JAPAN; Yohji Achiba, Tokyo Metropolitan Univ, Dept of Chemistry, Tokyo, JAPAN; Xinluo Zhao and Yoshinori Ando, Meijo Univ, Dept of Physics, Nagoya, JAPAN.

It is still in dispute whether the common structure of multi-walled carbon nanotube (MWNT) is concentric or scrolled. Thus, it is very interesting to measure the resonance Raman scattering of MWNTs because the Raman active breathing mode is an intrinsic vibrational mode of closed carbon nanotube. In this presentation, we will show results of the resonance Raman scattering of several kinds of MWNT samples fabricated by the electric arc method. In the case of high purity MWNT sample fabricated by carbon arc in hydrogen gas, we have successfully observed many breathing mode peaks with sharp resonance effect. Peak frequency is slightly higher than that of single-walled carbon nanotubes (SWNTs), and the resonance feature is quite similar to that of corresponding SWNTs. Further, it was confirmed that the breathing mode frequencies are consistent with observed diameters of core nanotubes by the transmission electron microscopy. On the other hand, in the case of MWNTs synthesized in helium gas, no breathing mode peak was observed.

U5.31

BORON ION IMPLANTATION INDUCED AMORPHIZATION AND FORMATION OF P-TYPE CONDUCTIVITY IN C₆₀ THIN FILMS. K.L. Narayanan and M. Yamaguchi, Toyota Technological Institute, Nagoya, JAPAN.

Ion Implantation in C₆₀ thin films has attained a renewed interest towards the fabrication of photovoltaic devices and hence understanding the properties of the fullerenes due to ion implantation is very important. High quality thin films with suitable optical and electrical properties are necessary for making solar cells. We have carried out boron ion implantation on C₆₀ thin films prepared by the molecular beam epitaxy(MBE) method. The idea of this study is to improve the electrical conductivity and realize the p-type material

using ion implantation. C₆₀ thin films of thickness 320 nm were prepared on glass substrates at a temperature of 150°C. These films were implanted with positive boron ions at a fixed energy of 80 keV to various doses in the range $1e12 - 1e15$ ions/cm². Raman scattering studies of the high dose implanted films reveal the formation of amorphous carbon layer as evidenced by the absence of the Raman modes of fullerenes. Fourier Transform Infrared studies also support the results by the Raman measurements. A dramatic increase in the conductivity of the films after high dose implantation is observed. Hall effect measurements further indicate the formation of p-type layer in the implanted region with a carrier concentration of about 1×10^{17} /cm³. The mobility of the films after boron implantation is found to be 1.6 volts/cm² - sec. The structural examination of the implanted films reveals the formation of amorphous carbon and hence we conclude the formation of p-type conducting amorphous carbon on boron ion implantation. We are now making photovoltaic devices with ion implantation induced p-type amorphous carbon with n-type silicon.

U5.32

SYNTHESIS AND THIRD-ORDER OPTICAL NONLINEARITY OF C₆₀ DERIVATIVE. Hongbo Li, Huiying Chen, Di Qiang, Dept of Chemistry, Peking Univ, Beijing, CHINA; Shufeng Wang, Wentao Huang, Hong Yang, Qihuang Gong, Dept of Physics, Peking Univ, Beijing, CHINA.

C₆₀ derivative, C₆₀-aminonitrile, C₆₀-dicyandiamide and their Fe³⁺ complex were synthesized. The results of FAB-MS and elemental analysis indicated that C₆₀-aminonitrile, C₆₀-dicyandiamide were multi-adduct products and the average number of aminonitrile-dicyandiamide molecule was five. C₆₀ and its derivatives' second-order hyperpolarizability γ were measured by femtosecond time-resolved optical Kerr effect. The results showed that the optical nonlinearity of C₆₀ was too low to be detected and an up-limit value of 9.0×10^{-35} esu was offered for its γ . On the other hand, large enhancement of optical nonlinearity for C₆₀-derivatives were observed. The γ value of C₆₀-aminonitrile was 1.2×10^{-32} esu and that of C₆₀-dicyandiamide was 4.4×10^{-32} esu. The origin of this extreme enhancement of the nonlinearity of fullerene was assigned to the formation of charge transfer. We compare this result with our previous work on the C₆₀-monoadduct: C₆₀-poly-aminonitrile, whose value of γ was 3.2×10^{-33} esu, and conclude that the γ value of C₆₀-monoadduct was not as large as its multiadduct. The γ value of C₆₀-dicyandiamide was larger than that of C₆₀-aminonitrile due to the longer conjugated chain and stronger ability of charge donor of dicyandiamide molecule. The γ value of Fe³⁺ complexes (Fe[C₆₀-aminonitrile] and Fe[C₆₀-dicyandiamide]) were about one fourth less than those of non-complex molecule. This result can be attributed to Fe³⁺ cation's ability of weakening the efficiency of charge transfer.

U5.33

THE SUPERCONDUCTIVITY FORMATION IN Cs₃C₆₀ CRYSTALS WITH RUBIDIUM IMPURITY. Dmitry V. Schur, Inst of Hydrogen and Solar Energy, Kiev, UKRAINE; Zinaida Matysina, Dnepropetrovsk State Univ, Dnepropetrovsk, UKRAINE; Svetlana Zaginaichenko, Vasily Pishuk, Inst for Problems of Materials Science of NAS, Kiev, UKRAINE; Boris Tarasov, Inst of New Chemical Problems, Chernogolovka, RUSSIA.

It has been found experimentally that in caesium fulleride Cs₃Φ (Φ=C₆₀) with the appearance of rubidium Rb atoms and formation of Cs₂RbΦ compound the superconductivity is manifested with critical temperature T_C=33 K. The theoretical investigation of temperature and concentration superconducting phase transition in Cs-Rb-Φ crystals is of interest to scientists. The calculation of crystal free energy is carried out on the basis of molecular-kinetic concept. The equations of equilibrium state are derived, these equations define the parameters of atomic and spin order in dependence on crystal temperature, its composition, energetic constants and determine the mutual influence of spin and atomic ordering. The critical temperature T_C of superconducting ordering is evaluated, its dependence on c_{Cs}, c_{Rb} concentrations of crystal components is determined. The deduced formula for T_C=T(c_{Rb}) dependence admits the possibility of increase of spin ordering temperature of Cs₃Φ crystal with appearance of rubidium Rb atoms in it and with increasing c_{Rb} concentration under condition of negative values of pairing energies J_{CsCs}, J_{CsRb} of conductivity electrons and more strong interaction between Cs, Rb atoms in comparison with Cs, Cs atoms pairs. By this means the presence of rubidium atoms stimulates the electron-phonon interaction of electrons, the process of their pairing, the formation of Cooper bosons and as a result of which the superconductivity manifestation (in agreement with experimental data). Using the experiments data for Cs₂RbΦ crystal, it has been done the estimation of energetic parameters J_{CsCs}, J_{CsRb} of electrons pairing at which the crystal transition to superconducting state is possible.

SESSION U6: POSTER SESSION:
APPLICATIONS OF AMORPHOUS AND
NANOSTRUCTURED CARBON: EMISSION,
ELECTRICAL, CHEMICAL, AND MECHANICAL

Chairs: Tatiana Allen and Otto Zhou
Tuesday Evening, November 30, 1999
8:00 P.M.

Exhibition Hall D (H)

U6.1

**CVD GROWTH OF CARBON NANOTUBES FOR FIELD
EMITTERS.** Gyula Eres, Y.Y. Wei, V. Merkulov and D.H. Lowndes,
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

For applications such as field emitters and other microelectronic devices, thin films are the most desirable form of carbon nanotubes. In this paper we report on optimizing CVD conditions for carbon nanotube growth on various substrates with respect to their field emission properties. CVD was conducted in a stainless steel chamber equipped with a substrate heater for decomposing the carbon-carrying source gas. Carbon nanotube production was evaluated as a function of the various substrate preparation methods and film growth parameters, including type of carbon source gas, type of catalyst, substrate temperature, and method of catalyst supply (pre-deposition or concurrent supply). A mechanism for CVD growth of carbon nanotube films based on these data will be described, and compared with models in the literature. Field emission from the nanotubes was measured by using a 25 μm diameter probe scanned in 3D. The effect of the probe size on the field emission parameters derived from these measurements will be discussed.

U6.2

**NANOTUBES VERSUS NANORODS : EFFECT OF Si AND N
INCORPORATION INTO CARBON NANOTUBES AND SiCN
NANORODS.** Padmakar Damodhar Kichambare, Cheng-Yen Wen,
Li-Chyong Chen, Center for Condensed Matter Sciences, National
Taiwan University, Taipei, TAIWAN; Kuei-Hsien Chen, Institute of
Atomic and Molecular Sciences, Academia Sinica, Taipei, TAIWAN;
Chin-Hsin Shen, Y.F. Chen, Department of Physics, National Taiwan
University, Taipei, TAIWAN; Fu-Gow Tarntair, Huang Chuang
Cheng, Department of Electronic Engineering and Institute of
Electronics, National Chiao Tung University, Hsinchu, TAIWAN.

Ever since the discovery of carbon nanotubes, there has been not only an enormous interest in preparing nano-structured materials other than carbon nanotubes but also using various alternative techniques to produce them. Recently nanorods of SiCN with hexagonal symmetry have been reported by our group. These nanorods preserved the same symmetry like SiCN crystals and exhibit superior emission current stability than pure carbon nanotubes. Within this context, it is thought worthwhile to incorporate Si and N in carbon nanotubes and investigate systematically the effect of Si and N addition on the morphological transformation and field emission characteristics of carbon nanotubes. Carbon nanotubes containing Si and N are grown on large area by microwave plasma enhanced chemical vapor deposition (MWPCVD) technique. Both nickel-coated silicon substrates and electron cyclotron resonance (ECR)-SiCN-coated silicon substrates are compared. Scanning electron microscopy (SEM) study reveals that these nanotubes are 7-10 μm in length and 0.1 μm in width. Auger electron spectroscopy (AES) study has been performed to determine the Si, C, and N content in it. These nanotubes still retain planer structure up to nitrogen concentration of 10 at.%. It is revealed from these studies that structural transformation are more pronounced at high nitrogen content. The effect of incorporation of Si and N in carbon nanotubes on the field emission properties of these nanotubes will be discussed and compared with SiCN nanorods.

U6.3

**DIELECTRIC PROPERTIES OF AMORPHOUS CARBON
NITRIDE FILMS.** M. Aono, S. Nitta, T. Itoh and S. Nonomura, Dept
of Electrical Engineering, Gifu University, Gifu, JAPAN.

Amorphous carbon nitride a-CN_x films are one of the promising materials for an application as thin insulator films [1]. a-CN_x films have higher resistivity and larger breakdown voltage than a-SiO₂, strength for water vapor penetration and theoretically good thermal conductivity, etc.. a-CN_x films have been prepared by the reactive radio frequency magnetron sputtering [2-4]. This process is hydrogen free method with a graphite target etched by the rf-plasma made from nitrogen molecule gas. Dielectric constants k were calculated from refractive indices n obtained from the UV-VIS transmittance spectra and from the VIS-ellipsometer. Dielectric constants k of a-CN_x films changes gradually from 3.57 for nitrogen content x=0.52 to 2.68 for x=0.86 depending on x. When a-CN_x becomes to chemically stoichiometric amorphous a-C₃N₄ (x=1.33), the dielectric constant is estimated experimentally as 1.82 at these optical frequency range.

The amorphous carbon nitride films prepared by the layer-by-layer method LL-a-CN_x shows smaller dielectric constant than a-CN_x made by the conventional reactive sputtering method. The characteristics of dielectric properties of a-CN_x 1 μm films in thickness were studied by using LCR meters. These measurements show the dielectric constants of a-CN_x as 7.0 ~ 7.5 at 1 MHz ~ 10 MHz. For a-CN_x with x=0.632, there is a peak in the dielectric dispersion curve at 30 MHz where the dispersion curve of a-CN_x increase with frequency. Dielectric constants of LL-a-CN_x with x=0.635 are 5.5 ~ 4.7 at 1 ~ 10 MHz which are smaller than a-CN_x. There is a peak for LL-a-CN_x in the dielectric dispersion curve at 30 MHz also, but the dispersion is different from a-CN_x and dielectric constants decrease with frequency. These values of dielectric constants for a-CN_x and LL-a-CN_x in the MHz frequency range are not small but could be controlled to become low dielectric constant materials. The resistivity of a-CN_x at room temperature are 10¹⁶ to 10¹⁷ $\Omega\text{-cm}$ for 0.52 < x < 0.68. Experimental dependence of resistivity on the nitrogen contents x can be extrapolated for a-C₃N₄ to 10²⁰ $\Omega\text{-cm}$. LL-a-CN_x have the larger resistivity of 10¹⁸ $\Omega\text{-cm}$ for the same nitrogen content of x=0.6. If sp³-bonding structure of carbon in the films increases, the resistivity could be controlled to higher values. [1] M. Aono, S. Nitta, T. Iwasaki, H. Yokoi, T. Itoh and S. Nonomura, Abstract of MRS spring meeting, (1999) 246.; [2] N. Takada, K. Arai, S. Nitta and S. Nonomura, Appl. Surf. Sci. 113/114 (1997) 274.; [3] S. Nitta, N. Takada, K. Sugiyama, T. Itoh and S. Nonomura, J. Non-Cryst. Solids 227-230 (1998) 655.; [4] T. Iwasaki, M. Aono, S. Nitta, H. Habuchi, T. Itoh and S. Nonomura, Diamond and Related Materials 8 (1999), 440-445.

U6.4

**PROPERTIES OF ION BEAM DEPOSITED FLUORINATED
AMORPHOUS CARBON FILMS (A-C:F).** H. Hofsäss, H.
Feldermann, S. Viridis, C. Ronning, II. Physikalisches Institut,
Universität Göttingen, GERMANY; R. Merk, Fakultät für Physik,
Universität Munster, GERMANY.

Fluorinated amorphous carbon films (a-C:F) may be of interest as low dielectric constant material and as a low stress diamondlike coating with specific wetting properties. We used mass-separated low energy ion beam deposition to grow thin films of fluorinated amorphous carbon films (a-C:F). Films were grown solely by deposition of 100 eV ¹²C⁺ and ¹⁹F⁺ ions on substrates kept at room temperature. The ion charge ratio was varied between pure ¹²C⁺ and [C⁺]:[F⁺] = 1:1, leading to films with a fluorine content varying between 0 at.% and 30 at.%. The films were characterized with Auger electron spectroscopy, FTIR and EELS. The film stress was analyzed by deposition on cantilever substrates. Under the chosen deposition conditions pure carbon films have a high sp³-bond fraction in excess of 80 % (tetrahedral amorphous carbon, ta-C) and a compressive stress of about 10 GPa. With increasing F content the film stress decreases dramatically, leading to almost stress free films for F concentrations above about 25 at.%. The electron density as determined by EELS in a-C₃F₁ films remains high, indicating a high fraction of carbon sp³ bonds. An analysis of the bond structure using XPS and ion beam analysis results are presented and possible applications of the films are discussed.

U6.5

AN AMORPHOUS DIAMOND-LIKE CARBON SENSOR DEVICE.
J.P. Sullivan, T.A. Friedmann, W.K. Schubert, D.R. Adkins, C.H.
Seager, M. Mitchell, R.G. Dunn and R.J. Shul, Sandia National
Laboratories, Albuquerque, NM.

Amorphous diamond-like carbon, a-D, has been used to create devices for use as chemical sensors. The devices are based on thin free-standing membranes of a-D that are vibrationally-excited. Excitation is achieved by passage of an AC current through a metal meander line that is patterned on to the membrane surface while the device is in the presence of a static magnetic field. The application of a thin organic or polymeric layer to the membrane surface permits the device to be used as a chemical sensor through measurements of adsorption-induced changes in membrane resonant frequency. The a-D material is uniquely suited for these devices because it is possible to finely tune the stress-state of the a-D film by changing the ratio of 4-fold to 3-fold carbon subsequent to deposition. Membranes that are stressed from slight tension through to slight compression may be created with membrane thickness from less than 60 nm to over 2000 nm and membrane areas exceeding 5 cm². The extremely high modulus, E_Y > 650 GPa, high fracture strength, and chemical inertness of a-D leads to mechanically robust and chemically-resistant membranes. The mechanical and physical properties of a-D membranes assessed by bulge test, burst test, and high energy and low energy photon absorption will also be discussed. Sandia is a multi-program laboratory operated by Sandia Corp., a Lockheed Martin Co., for the U.S. Dept. of Energy under contract DE-AC04-94AL85000.

U6.6
SINGLE-WALLED CARBON NANOTUBE-SUPPORTED PLATINUM CATALYST FOR SELECTIVE HYDROGENATION OF α,β -UNSATURATED ALDEHYDES. Vincenzo Lordi, Nan Yao and James Wei, Princeton Univ, Princeton Materials Inst and Dept of Chemical Engineering, Princeton, NJ.

Heterogeneous supported Pt catalysts are very important industrially for hydrogenation reactions. In the fine chemicals industry, particularly for the manufacture of certain flavorings, fragrances, and pharmaceuticals such as Vitamin A, Pt catalysts that serve to selectively hydrogenate the carbonyl function on α,β -unsaturated aldehydes are essential. It is known that the activity and selectivity of such catalysts is sensitive to the nature of the support material. Few studies, however, have focused on the role of the support in the function of the catalyst. Those studies that do address this issue often merely present a set of empirical results from numerous tests using several different supported catalysts. We have prepared a Pt catalyst supported on purified single-walled carbon nanotubes (SWNTs). Systematic characterization of the SWNT support both before and after metal loading is performed to better understand the structure and function of the support material. Unlike typical catalyst supports, SWNTs have a well-defined structure. In addition, this new catalyst has a relatively homogenous composition. The catalyst contains 10% loading of Pt by weight. The Pt particle size ranges from less than 1 nm in diameter to 10 nm, but the average size is 1-2 nm. Evidence indicates that the particles are chemically bonded to the surfaces of the bundled SWNTs. Each hexagonally-packed bundle contains on average 20-100 nanotubes. High-resolution transmission electron microscopy and electron energy loss spectroscopy were used to study the catalyst structure and the chemical bonds between the Pt particles and the carbon nanotube support. A preliminary kinetics investigation of the activity and selectivity of the catalyst for the selective partial hydrogenation of 3-methyl-2-butenal (prenal) to 3-methyl-2-butenol (prenol) is discussed.

U6.7
SYNTHESIS OF NOVEL MESOPOROUS CARBONS AND THEIR APPLICATIONS TO ELECTROCHEMICAL DOUBLE LAYER CAPACITORS. Taeghwan Hyeon, Seung M. Oh, Jinwoo Lee, Songhun Yoon, School of Chemical Engineering, Seoul National University, Seoul, KOREA.

The first synthesis of mesoporous carbonaceous materials with regular three-dimensionally interconnected pore arrays were achieved using inorganic mesoporous aluminosilicates as templates. Carbonization of phenol resin inside the mesopores of aluminum-MCM-48 followed by HF etching generated mesoporous carbon with regular 2 nm pore arrays. Using a similar approach, we have also prepared several other mesoporous carbons with regular nanometer size pore arrays. These mesoporous carbons were tested as the electrodes for electrochemical double-layer capacitors. The materials gave rectangular-shaped cyclic voltammograms, which are advantageous on the aspect of energy storage density and power density. This superior behavior compared to the conventional activated carbon results from the presence of three-dimensionally interconnected uniform mesopores. In this presentation, the synthesis, characterization, and electrochemical properties of these mesoporous carbon materials will be discussed.

U6.8
MOLECULAR DYNAMICS SIMULATIONS OF POLYMER-NANOTUBE COMPOSITES. Sarah-Jane V. Frankland, Donald W. Brenner, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

Because carbon nanotubes are very strong, flexible materials, there is the possibility of using nanotube fibers to enhance the mechanical properties of polymers. Understanding how the load transfer takes place between the polymer and the nanotube in the composite is key to the design of such materials. Molecular dynamics simulations of polymer/nanotube systems are in progress to address this issue by mapping out the stress/strain behavior of these systems. Issues being considered which may affect load transfer include the size of the nanotube, the effect of polymer/nanotube adhesion, and the importance of bent tubes.

U6.9
IMPROVEMENT OF OXIDATION DURABILITY OF DIAMOND FILM BY USE OF CERAMIC THIN FILM. H. Noguchi and T. Takarada, Faculty of Engineering, Gunma University, Kiryu-shi, Gunma, JAPAN.

Diamond is a promising material because of its excellent properties such as the highest Young's modulus and thermal conductivity and high transmittance for x-rays and from visible light to infrared rays. However, it is difficult for use in high temperature and oxidizing atmosphere, because diamond consists of carbon. In this study, in

order to suppress the oxidation damage of diamond film, we have proposed the diamond/SiC or SiCN double layer structure. Silicon substrate surface of 100-mm-diameter was pretreated in a fluidized bed of diamond particles to obtain a high nucleation density ($3.4 \times 10^{10} \text{ cm}^{-2}$) of diamond sites. Diamond film was deposited using a magnetically enhanced microwave plasma chemical vapor deposition (CVD) system. The SiC or SiCN film was deposited in the r.f. (13.56 MHz) magnetron sputtering system on polished diamond film. The oxidation characteristics of the coated diamond film prepared were examined under the annealing conditions of 10 vol.% oxygen and the temperatures from 600 to 1000 Å. The evaluation, i.e., change in mass, crystallinity, and before and after the annealing, was performed using TG system, XRD, and SEM, respectively. The oxidation rate of the diamond film depended on the thickness and material of the coating film. The protective performance of SiCN film was more effective than that of SiC film, because of its high adhesive to diamond surface. The diamond film coated with 0.6 μm SiCN film showed no damage for annealing temperature of 800 Å for 300 min.

U6.10
AN ELECTROCHEMICAL IMPEDANCE STUDY AND LASER IRRADIATION EFFECTS ON THE ELECTRONIC STRUCTURE OF SILICON CONTAINING DIAMOND-LIKE CARBON COATING. Costas G. Fountzoulas, Jack V. Kelley and James D. Kleinmeyer, Army Research Laboratory, Weapons Materials Directorate, APG, MD; Garry P. Halada, State University of New York at Stony Brook, Stony Brook, NY.

Hard, adherent and lubricious silicon containing diamond-like carbon coating (Si-DLC) was synthesized by 40 keV Ar⁺ ion beam assisted deposition (IBAD) of tetraphenyl-tetramethyl-trisiloxane oil on two, polished and 600 grit finish (unpolished), 5 cm by 5 cm by 0.64 cm thick 4340 steel substrates. The thickness of the coating on the 600 grit finish and on the polished steel substrate was 2 μm and 4 μm respectively. The corrosion resistance of the Si-DLC coating was evaluated by Electrochemical Impedance Spectroscopy (EIS). A 0.005N concentration sodium chloride (NaCl) solution was used as the electrolyte for the corrosion evaluation of the Si-DLC coating. A small excitation amplitude of 10mV was also applied. Low frequency impedance data of each of the coatings were compared with those of bare steel. The Si-DLC coating deposited on the polished substrate performed slightly better than the one deposited on the unpolished surface. However, overall the Si-DLC coating does not appear to offer very much corrosion protection to the steel. This was mainly attributed to the presence of pinholes in the coating. The pinhole density in the Si-DLC coating was examined and evaluated with the aid of optical and photo tunneling microscopy. The pinhole density in the Si-DLC coating deposited on the polished substrate was smaller than the pinhole density of the coating deposited on the unpolished substrate. Furthermore, to study the effect of radiation on the electronic structure of the Si-DLC coating, three Si-DLC coatings synthesized by 40 keV Ar⁺ IBAD of tetraphenyl-tetramethyl-trisiloxane oil on silicon substrates at oil precursor temperatures of 125°C, 140°C and 155°C, were irradiated by a 355 nm wavelength, 0.37 Watts, pulsed YAG Laser at 35 kHz. Before irradiation the valence band of the films synthesized at 140°C and 155°C was the same but different than the valence band of the film synthesized at 125°C. After irradiation the valence band of all films was the same. Tribology results, ways to minimize the pinhole density in the Si-DLC coating and irradiation results will also be discussed in detail.

U6.11
EXACT ANALYTICAL SOLUTION FOR FILM GROWTH ON OXIDIZED GLASSY CARBON - THEORETICAL AND EXPERIMENTAL ANALYSIS. A. Braun, M. Bärtsch, B. Schnyder, R. Kötz, Paul Scherrer Institute, Dept. of General Energy Research, Villigen PSI, SWITZERLAND.

Glassy Carbon (GC) sheets are currently utilized as bipolar electrodes for electrochemical double layer capacitors (EDLC)¹. GC can be regarded as a network of graphitlike nanocrystals, which enclose voids of not more than one or two nanometer in size, yielding an apparent porosity of around 30%. For utilization as EDLC electrodes, the pores must be opened by an activation process, which is usually performed by oxidation. The oxidation creates a film with open pores on top of the GC with closed pores. One convenient process is thermochemical oxidation. As the film growth is superimposed by a shrinking of GC due to burn-off, mathematical modelling of the growth process is substantially complicated. However, it turns out that the system *thermochemical oxidation of GC* represents an exactly solvable growth problem, when the LambertW function is applied. We present a mathematical model for the film growth on flat shrinking GC samples and a simple exact analytical expression for the film thickness as a function of oxidation time and process and materials parameters. Experimental data obtained from GC samples with different structure oxidised at various temperatures and gas concentrations at different time are also presented and compared with the theoretical

predictions. Financial support by the Board of the Swiss Federal Institute of Technology and fruitful discussions with Dr. R. Struis (PSI) are gratefully acknowledged. [1] A. Braun, M. Bärtsch, F. Geiger, B. Schnyder, R. Kötz, O. Haas, M. Carlen, T. Christen, C. Ohler, P. Unternährer, E. Krause. MRS Symposium Proceedings Series, Vol. 575, CC.7.3, Spring Meeting, San Francisco (1999).

SESSION U7: POSTER SESSION:
AMORPHOUS CARBON GROWTH, STRUCTURE,
AND PROPERTIES

Chairs: Tatiana Allen and Otto Zhou
Tuesday Evening, November 30, 1999
8:00 P.M.

Exhibition Hall D (H)

U7.1
MOLECULAR-DYNAMICS SIMULATIONS OF STEADY STATE GROWTH OF ION-DEPOSITED TETRAHEDRAL AMORPHOUS CARBON FILMS. Hans-Ulrich Jäger, Forschungszentrum Rossendorf e.V., Institut f. Ionenstrahlphysik und Materialforschung, Dresden, GERMANY; Karsten Albe, University of Illinois at Urbana-Champaign, Materials Research Laboratory, Urbana, IL.

Atomic-scale modeling of ta-C thin film deposition by molecular dynamics simulations is an indispensable tool for understanding growth, structure and properties of diamond-like carbon in detail. Even if much progress has been achieved in recent years, simulations comparable to experiments are for several reasons still an enormous challenge: A large number of impacts has to be calculated in order to achieve steady-state growth conditions. Long time intervals between individual impacts, which correspond to real ion fluxes, are necessary to allow for full structural relaxation of the growing film. The simulation ensemble has to be large enough, so that the dynamics of atoms in the growing film is not affected by external thermostats. Finally, force-field calculations are necessary, which are computationally efficient, but allow for a realistic description of the chemical specificities of the growing amorphous carbon structures. In this contribution we present classical molecular-dynamics simulations, which try to balance the above-named criteria and deliver results directly comparable to experiments. All simulations were performed on base of the Brenner-potential, but with a slightly modified interaction radius, which corrects several shortcomings of the original form. Using this computationally efficient and chemically accurate potential function we have calculated the impacts of 1200 carbon atoms with 15 ps relaxation time after every event. In contrast to previous works our simulations were performed for realistically thermalized targets and yield steady-state film structures, which were carefully analyzed. The sp^3 -contents for the deposited ta-C films vary between 58 % and 90 % for the C^+ ion energies $E = 30$ -80 eV and are in good agreement to experimental findings.

U7.2
ELECTROSTATIC MEASUREMENT OF PLASMA PLUME DYNAMICS IN PULSED LASER EVAPORATED GRAPHITE. R.M. Mayo, J.W. Newman, Department of Nuclear Engineering, North Carolina State University, Raleigh, NC; A. Sharma, J. Narayan, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC; Y. Yamagata, Department of Electrical and Computer Engineering, Kumamoto University, Kumamoto, JAPAN.

Thin films of Diamond-Like-Carbon (DLC) are routinely produced by pulsed laser evaporation (PLE) of graphite targets. The optical, electrical, and mechanical properties of such films make them rather attractive for applications from wear resistant coatings for optical components to substrate material for advanced semiconductor devices. Pulsed laser deposition (PLD) has numerous advantages, particularly, the presence of energetic species in the plasma results in a large fraction of sp^3 bonded carbon. This study concentrates on electrostatic (Langmuir) probe measurements in the carbon PLE plume to investigate plume dynamics and, in future work, correlate against film properties. The experimental facility for PLE at NCSU (J. Appl. Phys., **73** (1993) 316) consists of a spherical vacuum chamber ($< 10^{-7}$ Torr), a Lambda Physik KrF (248 nm) excimer laser with ~ 45 ns pulse width (25 ns FWHM) delivering typically 2-3.5 J/cm² to a rotated graphite target at 45° incidence, and a substrate mounted 5-10 cm from the target. Normal to the target, on a sliding vacuum seal, is installed a triple Langmuir probe for the studies discussed herein. The probe consists of three cylindrical Tungsten tips (10 mil dia., and 5 mm in length) and is biased to -7 to -10 V to reach ion saturation. Time resolved (currently at 5Ms/s) measurements of n_e , T_e , and floating potential are recorded at probe-target separation of 1, 3, and 5 cm. Beyond this separation, ion saturation signal strength is greatly diminished. Preliminary results indicate electron densities on the order of 10^{12} - 10^{15} cm⁻³ and

electron temperatures ~ 0.5 -3.0 eV at 1 cm from the target surface. Plasma density is often observed to increase initially with probe-target separation distance before decreasing, a result thus far attributed to slightly off-center probe tip occulting by the highly forward directed plume. Plume front energy is estimated to be in excess of 150 eV, by peak density signal arrival time at several probe-target separations, and is constant with distance although an increasing function of laser energy and decreasing with fill gas pressure, as will be presented. Increased fill gas density delays ion saturation signal arrival time and reduces magnitude as expected. In the presence of intermediate background Ar and N₂ fill (100-300 mTorr) a second, long delayed feature in the n_e signal is observed. This is a possible signature of heavy cluster formation, although formation and ionization mechanisms are currently under investigation.

U7.3
DEPOSITION AND ANNEALING STUDIES OF DIAMOND-LIKE CARBON GROWN BY MOLECULAR BEAM DEPOSITION (MBD). Oliver C. Goetzberger, Nobuaki Kojima, Aurangzeb Khan and Masafumi Yamaguchi, Toyota Technological Institute, Nagoya, JAPAN.

Carbon-based materials are attractive for electronic device application. For this end, it is necessary to understand and control their physical properties. In the paper we are presenting the characteristic of diamond like carbon grown by MBD. We have analyzed the films by different techniques like X-ray Photoelectron Spectroscopy, Raman Spectroscopy, UV-VIS Spectroscopy. For the deposition we have used an ULVAC MBE system which is electron beam assisted. The film deposition was carried out on glass substrates at room temperature. For the optical absorption we took an UV/VIS spectra between 300 and 1100nm. We calculated a Tauc Plot. Optical absorption measurement indicates that our typical films have an optical band gap of 1.5eV. We are also discussing the optical absorption coefficient. In the XPS we have found 41% sp^3 bonded carbon and 59% sp^2 bonded carbon. The content of sp^3 bonded carbon is decreasing as a function of depth. Inside the film we have found no sp^3 bonded carbon. In the Raman spectra we can observe the G-peak at 1555cm⁻¹. The result is correlated to the result in XPS. The annealing measurements (200 to 500°C for 1 hour) show a linear decrease of the optical band gap down to 1.1eV. Also the sp^3 content is decreasing down to 28%. We have studied the annealed samples with XPS depth profile measurements. The 200°C annealed sample shows a disorder of the sp^3 content inside the film. If we increase the temperature up to 500°C then the sp^3 content is fluctuating around 28%. The Raman Spectra shows a shift of the G-Peak to higher values. The peak at 1077cm⁻¹ is disappearing. These results suggest the possibility of controlling physical properties such as optical band gap, electrical conductivity and so on with annealing.

U7.4
DIRECT ION BEAM DEPOSITION OF DIAMOND-LIKE FILMS FROM RF INDUCTIVELY COUPLED (IC) PLASMA SOURCE: MECHANICAL, ELECTRICAL AND OPTICAL PROPERTIES. Boris Druz, Isaak Zaritskiy, Kurt William, Alan Hayes, Veeco Instruments, Inc., Plainview, NY; Vasily Poljakov, Alexandr Khomich, Institute of Radio Eng. & Electronics, Moscow, RUSSIA; Xiudong Li, Bharat Bhushan, The Ohio State University, Columbus, OH.

Diamond-like carbon (DLC) films were deposited on various substrates using highly reproducible direct ion beam deposition from RF IC CH₄ plasma source¹. Combinations of gases such as CH₄, CH₄-N₂ were used to form plasma. The mechanical, electrical and optical properties of the films were examined as a function of deposition conditions and N₂ content in gas composition. A small amount of N₂ (6-8 sccm) did not markedly change hardness and stress, while electrical conductivity was significantly increased. In addition, a small amount of N₂ improved tribological performance of the films reducing amount of debris and wear track size. Introduction of high N₂ flow into the system significantly deteriorates value of these parameters. It was found that N₂ essentially increases absorption coefficient, and reduces optical band gap. Analysis of the experimental results shows that observed effects can be explained by incorporation of N₂ into carbon-strained network that induces structural changes and, in turn, leads to an increase of sp^2 fraction in the DLC films. For investigation of the bulk and surface electrically active defects, charge deep level transient spectroscopy (Q-DLTS) technique was used. The density, activation energies and capture cross-sections of the bulk and surface defects in the DLC films with different N₂ content were found. The role of the point defects in the DLC films is discussed.

U7.5
RAPID PHOTO-THERMAL CHEMICAL VAPOUR DEPOSITION OF AMORPHOUS CARBON FROM DIODOMETHANE. Mikael Lindstam, Mats Boman, Uppsala University, The Angstrom

Laboratory, Dept of Inorganic Chemistry, Uppsala, SWEDEN; Klaus Piglmayer, Johannes Kepler University, Institute of Experimental Physics, Department of Applied Physics, Linz, AUSTRIA.

A novel method for deposition of amorphous carbon were investigated. The combination of thermal processing and quantum photo effects show new interesting growth conditions that will be discussed. The halogen lamp was focused onto the substrate surface and the temperature was monitored by a laser pyrometer. The deposition process was investigated as a function of lamp power, operating pressure and substrate material. The films were analysed with Raman spectroscopy, infrared spectroscopy, X-ray photon spectroscopy and atomic force microscopy. Despite the rapid growth, 2.5 nm/s, the carbon films were smooth and had good adhesion.

U7.6
FLUORINATED DIAMOND-LIKE CARBON FILMS PRODUCED BY PLASMA IMMERSION ION PROCESSING TECHNIQUE. M. Hakovirta, D.H. Lee, X-M. He, M. Nastasi, Los Alamos National Laboratory, Los Alamos, NM.

Fluorinated diamond-like carbon (FDLC) films were deposited with plasma immersion ion processing (PIIP) technique. Both pulsed glow discharge and inductive rf plasmas from acetylene and hexafluoroethane gases were used for the depositions. In this paper, composition, tribological, and un-wetting properties of these films will be reported as a function of fluorine content and the issues for incorporation of fluorine into DLC with PIIP technique will be discussed.

U7.7
EFFECTS OF CF₄ ADDITION ON THE GROWTH OF AMORPHOUS CN_x FILMS BY PLASMA DECOMPOSITION OF CH₄-N₂ GAS MIXTURES. Takao Inokuma, Hironobu Matsumoto, Yoshihiro Kurata, Seiichi Hasegawa, Kanazawa Univ, Dept of Electrical & Computer Eng, Kanazawa, JAPAN.

In the deposition of CN_x films using CH₄-N₂ plasma, it is known that the presence of hydrogen radicals hinders growth of the films because of their high etching activity. To control the concentration of such hydrogen radicals, supply of fluorine radicals to the plasma is considered effective: When fluorine radicals exist together with hydrogen radicals, the hydrogen radicals should be partially eliminated through the formation of stable HF molecules. In this paper, we focus on the growth of amorphous (a-) CN_x films by plasma-enhanced chemical vapor deposition (PECVD) using CH₄-N₂ gas mixtures, and investigate effects of the addition of CF₄ gas as a source of fluorine radicals.

Sample films were deposited by varying a flow rate ratio $R_{CF} = [CF_4] / ([CH_4] + [CF_4])$ from 0 to 1 under a fixed flow rate of [CH₄] + [CF₄] at 1.67 sccm. The flow rate of N₂ was 8.33 sccm. The deposition temperature and pressure were 200°C and 14 Pa, respectively. The samples obtained were characterized by x-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR).

When CF₄ was added, the deposition rate of a-CN_x films steeply increases with increasing R up to ~0.3, and then it decreases slowly. From the results of XPS, it was found that the nitrogen content, x, of the films was increased from 0.22 to 0.36 when R_{CF} was increased from 0 to 0.3. The inclusion of fluorine atom into the samples was less than 5%. The FTIR spectra showed strong enhancement of the absorption bands related to various forms of C-N bonding by the CF₄ addition. Based on these results, it is suggested that the addition of CF₄ reduces hydrogen radicals in the plasma and enhances the growth and nitrogen inclusion.

U7.8
EFFECTS OF O₂ GAS ADDITION ON DIAMOND LIKE CARBON FILM DEPOSITION. Norikazu Nakamura, Shoichi Suda, Masayuki Takeda, Tsukasa Itani and Kazuaki Kurihara, Fujitsu Laboratories Ltd, Inorganic Materials and Polymers Laboratory, Kanagawa, JAPAN.

The role of O₂ gas addition in deposition of Diamond-like Carbon (DLC) film was studied. The influence of O₂ gas mixing ratio on DLC film quality was investigated using dc magnetron sputtering method with solid graphite target and Ar, CH₄ and O₂ mixing gas. O₂ mixing ratio was changed between 0% to 50%. Temperature dependence was also investigated. The film quality was evaluated using Raman spectroscopy and XPS. Id/Ig ratio of Raman spectrum increase with increasing O₂ mixing ratio. B/A ratio, which is the ratio of peak intensity including background and without background, decrease over 30% O₂ content. It seems that O₂ gas react selectively with polymeric components in DLC film.

U7.9
EFFECT OF ARGON ADDITION ON NITROGEN CONTAINING CARBON FILMS PREPARED BY HOT CARBON FILAMENT

CVD. Yoshihisa Watanabe, Shinobu Ohnita, Nobuaki Kitazawa and Yoshikazu Nakamura, National Defense Academy, Department of Materials Science and Engineering, Kanagawa, JAPAN.

Nitrogen containing carbon thin films were synthesized on silicon single crystal substrates by hot carbon filament CVD in nitrogen and argon atmosphere, and the effect of argon addition on film structure and properties was studied by changing the partial pressure of argon under the total pressure of 100 Pa. Depositions in pure nitrogen or argon atmosphere were also performed. The synthesized films were characterized by scanning electron microscopy, atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. XPS studies show that the films are composed of carbon and nitrogen, and extraneous peaks due to contamination are hardly observed. Observations by AFM reveal that the average roughness of the films decreases with the amount of argon addition. It is also found from the Raman spectroscopy that two broad peaks corresponding to the G band and the D band are observed in the films prepared in the nitrogen rich atmosphere, while the films prepared in the argon rich atmosphere tend to show a single peak. It is concluded that argon addition during synthesis has a marked effect on the growth of nitrogen containing carbon films.

U7.10
ELECTRICAL AND ELECTROCHEMICAL PROPERTIES OF a-C:N FILMS. Yu. V. Pleskov, M.D. Krotova, Frumkin Institute of Electrochemistry, Moscow, RUSSIA; V.I. Polyakov, A.V. Khomich, A.I. Rukovishnikov, Institute of Radio Engineering and Electronics, Moscow, RUSSIA; B. Druz, D. Kania, A. Hayes, Veeco Instruments Inc., Plainview, NJ.

Nitrogen-doped amorphous carbon (a-C:N) films, 200 to 500 nm thick, have been fabricated on conductive n-type silicon and glass substrates using direct ion beam deposition from an RF inductively coupled methane/nitrogen plasma source [1]. The increasing of nitrogen/methane ratio in the gas mixture lead to systematically decreasing of electrical resistivity and Tauc bandgap of the a-C:N films. The charge-based deep level transient spectroscopy was used for study of point defects (trapping centers, TC) in the films. The concentration, activation energy, and capture cross-section of the TC were determined.

Electrochemical AC impedance and kinetics at the a-C:N electrodes were studied in contact with 1 M H₂SO₄ electrolyte solution containing Fe(CN)₆^{3-/4-} redox system. From the impedance measurements at the electrolytic contact, the films' resistivity was determined, which coincides, within a factor of 1.5-2, with that obtained from the DC measurements with metal contacts. When the Tauc gap of a-C:N decreased from 1.3 to 0.6 eV, the charge transfer at the a-C:N film/redox electrolyte interface was facilitated. The films proved to be stable electrodes for electrochemical applications. This work was supported in part by the Russian Foundation for Basic Research (projects 98-03-32057 and 98-02-16679).

1. B. Druz, E. Ostan, S. Distefano, A. Hayes, V. Kanarov, V. Polyakov, A. Rukovishnikov, N. Rossukanyi, A. Khomich, Diamond and Related Mater. 7 (1998) 965-972.

U7.11
ELECTRICAL AND STRUCTURAL PROPERTIES OF CARBON-NITROGEN THIN FILMS. R. Kurt, R. Sanjines, A. Karimi, Department of physics, Swiss Federal Institute of Technology (EPFL), Lausanne, SWITZERLAND.

To investigate the role of nitrogen in the C-N chemical bonding and the formation of CN_x phases, several carbon thin films containing variable concentration of nitrogen were grown onto the Si (100) substrates using magnetron sputtering in Ar/N₂ discharge. Variation of the sputtering conditions such as working pressure, substrate voltage, and N₂/Ar ratio in the discharge plasma led to a wide range of coating properties. Grazing incidence X-ray diffraction and TEM electron diffraction confirmed that the deposits are almost amorphous but contain small crystalline CN_x compounds. Size of CN_x crystals did not exceed 2-3 microns and their structure was found to correspond to the large number of suggested CN_x phases that exist in the literature. [N]/[C] ratio of the films as measured by RBS did not exceed x = 0.6. Special attempts were focused on the electrical properties of the films determined over a temperature range varying between the room temperature and 10 K, using four-point probe method under vacuum. For these measurements, CN_x films were deposited onto the silicon substrate covered with a layer of isolating SiO₂ to avoid any effect of substrate. The electrical resistivity of all deposits was increased when decreasing measuring temperature thus, confirming semiconducting behavior of CN_x films. The lowest resistivity was measured for the films free of nitrogen, whereas the films with 30-35%N₂ revealed the strongest semiconducting properties. In this paper, the temperature dependency of the electrical resistivity of CN_x films will be analyzed according to the established laws of the transport theory. The results will be discussed with

respect to the mechanical properties determined using either the biaxial tensile testing of free standing films (bulge test) or the nanoindentation of the films adhering onto their substrate

U7.12

MD-STUDY OF NITROGEN INCORPORATION INTO TETRAHEDRALLY BONDED AMORPHOUS CARBON (TA-C). Thomas Koehler, G. Jungnickel, Thomas Frauenheim, Universitaet Gesamthochschule Paderborn, Fachbereich Physik, Paderborn, GERMANY.

We discuss the properties of nitrogen impurities inside tetrahedrally bonded amorphous carbon. In contrast to previous studies on this subject we have incorporated up to 11 at.% N atoms in models of the disordered carbon material before the structural evolution which is simulated by annealing of a high-temperature phase. We observe the formation of local configurations that are self-trapping and, therefore, would not change the conductivity of the structure at all. Other local geometries which potentially would be useful in doping appear to be slightly more favourable as the non-doping sites but are found to be de-activated by charge migration away from the dopant site. Systematic studies of the carbon host properties as a function of the nitrogen concentration show that nitrogen tends to lower the connectivity of the network and promotes the formation of 3-fold carbon atoms, which limits electronic application.

U7.13

TRANSPORT PROPERTIES OF AMORPHOUS DIAMOND LIKE CARBON FILMS DOPED WITH BORON. T. Allen, C.A. Hixson, Univ of Tennessee, Chattanooga, TN; C. Cheney, G. Lupke, N.H. Tolk, Vanderbilt Univ, Nashville, TN; F. Gaspari, S. Zukotynski, Univ of Toronto, CANADA.

Amorphous hydrogenated diamond-like carbon (DLC) films prepared by the saddle-field glow discharge technique have been studied. Deposition of undoped films was carried out using ultra-pure methane. The setup also allows doping the films from the gas phase during deposition. Doping with boron has been proved to be controllable and electrically effective. The samples are p-type and exhibit a thermally activated conductivity in the temperature range 300-500 K. The data on hole concentration and mobility obtained from Hall effect measurements will be presented. Changes in transport properties of the samples resulted from wavelength selective free-electron laser treatment will be discussed.

U7.14

BAND OFFSETS IN UNDOPED AND NITROGENATED TETRAHEDRAL AMORPHOUS CARBON (TA-C)/SILICON HETEROJUNCTIONS. Nalin Rupesinghe, Gehan Amratunga, Univ of Cambridge, Dept of Engineering, Cambridge UNITED KINGDOM; Jamie Cole, Peter Weightman, Univ of Liverpool, Dept of Physics and IRC for Surface Science, Liverpool, UNITED KINGDOM.

Tetrahedral amorphous carbon (ta-C) thin films have been found to be potentially good candidates for cold cathodes for field emission display applications. However, there has been a debate as to whether the emission is limited by the ta-C surface or the heterojunction barrier at the back contact. Understanding the field emission mechanism has been hindered by the lack of any directly measured data on the energy band offset between ta-C and Si. Here we report results from direct in-situ XPS measurements on the band offset between ta-C and Si. Ta-C films were deposited by a filtered arc attached to an UHV XPS chamber. Analysis of the data shows a ta-C valence band offset of $0.8\text{eV} \pm 0.05$ on n-type Si and an offset of $0.1\text{eV} \pm 0.05$ on p-type Si. The Fermi level of the as deposited ta-C was found to be 0.3eV above the valence band, confirming its p-type nature. Nitrogen doping of ta-C has been observed experimentally. Here we confirm that the Fermi energy moves towards the mid-gap with the introduction of small amounts of nitrogen in the ta-C matrix. The implications of the heterojunction energy barrier heights for field emission from ta-C are also discussed.

U7.15

ELECTRICAL BEHAVIOR OF PURE AND COPPER DOPED DIAMONDLIKE CARBON PREPARED BY PULSED LASER DEPOSITION. Q. Wei¹, A.K. Sharma², S. Yarmolenko¹, J. Sankar¹ and J. Narayan², NSF Center for Advanced Materials and Smart Structures. ¹Dept of Mechanical Engineering, North Carolina A&T State University, Greensboro, NC, ²Dept of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

We have prepared pure diamondlike carbon films and copper doped diamondlike carbon films through pulsed laser deposition. The Cu concentration is around 1.0 atomic percent. Electrical conduction studies were carried out on the films to understand the electrical transport mechanism. It was found that both pure DLC and Cu doped DLC is of p-type conduction. The Cu doped DLC films

exhibited $T^{-1/2}$ temperature dependence, rather than the $T^{-1/4}$ dependence (Mott-Davis law). This dependence was observed within a wide temperature range (from liquid He temperature to near room temperature). The $T^{-1/2}$ dependence was explained on the basis of the Efros-Shklovskii theory which considers the long-range Coulomb interactions between localized states.

U7.16

Z-CONTRAST IMAGING AND EELS ANALYSIS OF CHROMIUM DOPED DIAMOND-LIKE CARBON. X. Fan, E.C. Dickey, Department of Chemical and Materials Engineering, University of Kentucky, Lexington, Kentucky, KY; S.J.Pennycook, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Diamond-like carbon (DLC) has attracted considerable interest with a variety of potential applications. A new class of amorphous films has been produced recently by incorporating metals within the carbon network. The electrical conductivity of these films varies over a wide range, however nonlinearly with the metal concentration. This response is attributed to cluster formation of the metals. Such nano-phase metal clusters encapsulated by an inert matrix can offer interesting applications, for example as nano-electrodes used in electrochemistry. It is therefore fundamentally important to understand the formation of metal clusters within diamond-like carbon matrices. In this study we investigated chromium-doped diamond like carbon films grown by a plasma chemical deposition technique. The doping of chromium was performed by co-evaporation of chromium into the reactor volume while growing the carbon film. The Z-contrast images were taken using a VG HB603U STEM and EELS spectra were taken using a VG HB501 STEM and a Philip CM200 TEM. We use Z-contrast STEM imaging to directly observe metal cluster formation and distributions within the chromium-doped carbon films. At low doping ($\sim 6\%$ Cr), Cr is uniformly distributed; at high doping ($\sim 12\%$ Cr), Cr-rich clusters are formed. Using electron energy loss spectroscopy (EELS), we find that the Cr clusters tend to be metallic-like at low doping levels and carbide-like at high doping levels according to the Cr L_{2,3} white line ratios. The carbon is more diamond-like at low doping and more graphite/carbide like at high doping according to the sp^2/sp^3 electron percentage measurements.

U7.17

PROBING SOLID CARBON STRUCTURE USING RAMAN SPECTROSCOPY. Joseph Libera, Yury Gogotsi, University of Illinois at Chicago, Dept of Mechanical Engineering, Chicago, IL.

An intensive effort has been undertaken to understand the hydrothermal behavior of solid carbon materials with the goal of diamond synthesis as well as the synthesis of many other novel solid carbon materials. The Raman signature of solid carbon is very sensitive to its structural properties but a comprehensive explanation of all the spectral features is lacking in the literature. It is observed that most carbon substances with the exception of the purest crystals of diamond and graphite exhibit structural variation as revealed by micron sized laser probes. A recently compiled Raman spectral database of solid phase carbon materials has been constructed to provide a consistent correlation of spectral features to solid carbon structure. The materials include single crystal and powdered graphites, glassy carbon, hydrogen plasma treated graphite, and synthesized carbon films from halogen etching of SiC and hydrothermal experiments in the C-O-H and C-O-H-metal systems. As many as 11 peaks occur in pure carbon substances with an additional 4 peaks in carbons suspected to contain hydrogen. Of particular interest are the spectra of solid carbons before and after treatment, which through etching isolate selective structural components. This paper summarizes all outstanding issues regarding the Raman spectra of solid carbons through the comprehensive examination of a large sample of solid carbon materials. Data were collected using 514.5 nm laser excitation over the wavenumber range $300\text{-}3500\text{ cm}^{-1}$.

U7.18

DENSITY AND SP3 CONTENT IN DIAMOND-LIKE CARBON BY X-RAY REFLECTIVITY AND ENERGY LOSS SPECTROSCOPY. A LiBassi, B.K. Tanner, Physics Dept, Durham University, UK; A.C. Ferrari, V. Stolojan, L.M. Brown, J. Robertson, Engineering Dept, Cambridge University, UK.

The bonding in diamond-like carbon films is defined by 2 key parameters, the sp^3 fraction and the hydrogen content. The standard method to obtain sp^3 content by Electron Energy Loss spectroscopy (EELS) from the size of the 285 eV peak. EELS also gives the valence plasmon energy, from which we can derive the density, which can be a useful cross check on the sp^3 fraction. However, there is a desire for a more rapid, non-destructive technique than EELS for this information. Grazing angle x-ray reflectivity (XRR) is a well established, quantitative, non-destructive technique to give the electron density and thickness of layers. We find that the bulk mass density of optimised tetrahedral amorphous carbon (ta-C) is 3.26

gm/cm³, for which EELS found a sp³ fraction of 85%. Such data can be used to benchmark the dependence of sp³ fraction on density for hydrogen-free DLCs. On hydrogenated ta-C (ta-C:H) deposited by high plasma density reactors such as the plasma beam source (PBS) or the electron cyclotron wave resonance (ECWR) reactor from acetylene source gas, we find a density of 2.35 gm/cm³, 75% sp³ and ~30% hydrogen. The density is much lower than previously given. It is much more consistent with the space filling of hydrogen in the network. This data provides a similar validation for density and sp³ EELS data for hydrogenated DLCs. XRR can also reveal internal layering in films, and indeed less dense sp³ layers are found at the surface of ta-C films, but no such layers are found so far on ta-C:H films. The variation of layer depth can be a significant factor in the apparent variation of bulk sp³ content with incident ion energy.

U7.19

TAILORING SP²/SP³ CARBON RATIO IN HYDROGENATED DLC AND HYDROGEN-FREE T_xA-C_{1-x} - A COMPARATIVE STUDY. Minseo Park, P.T. Barletta, R.M. Pope, S.M. Camphausen, V. Sakhrani, J.T. Smith, D.E. Jonsen, R.J. Nemanich, R.C. Sanwald, and J.J. Cuomo, Dept. of Materials Sci. and Eng., and Dept. of Physics, North Carolina St. Univ., Raleigh, NC.

A set of hydrogenated diamond-like carbon (DLC) and hydrogen-free t_xa-C_{1-x} films were prepared by various processing techniques, namely; plasma enhanced chemical vapor deposition, ion beam sputtering, filtered cathodic arc deposition, and End-Hall source assisted deposition. The processing parameters which appear to have the greatest effects on the sp²/sp³ carbon ratio are presented. Stokes and anti-Stokes Raman scattering, and electron energy loss spectroscopy (EELS) were used to assess the bonding configuration of the material. An insight into the mechanism of carbon hybridization is discussed.

U7.20

STRUCTURE AND PHOTOLUMINESCENCE OF HYDROGENATED AMORPHOUS CARBON FILMS PRODUCED BY USING AROMATIC HYDROCARBON SOURCE. Jun Xu, Tianfu Ma, Wei Li, Li Wang, Nanjing Univ, National Lab of Solid State Microstructures, Nanjing, CHINA; Zhifeng Li, Shanghai Inst of Technical Physics, National Lab for Infrared Physics, Shanghai, CHINA; Kunji Chen, Nanjing Univ, National Lab of Solid State Microstructures, Nanjing, CHINA.

Hydrogenated amorphous carbon (a-C:H) film and its-based materials are becoming increasingly important for various device applications and their structures and optical properties are quite different depending on the fabrication technique and conditions. It has been reported that, by using aromatic hydrocarbon source - xylene (C₈H₁₀), an intense blue light emission can be observed from hydrogenated amorphous silicon-carbon films at room temperature. In this report, a series of a-C:H films were produced in PECVD system by using xylene as a carbon source. The deposited samples were characterized by using FT-IR, Raman and photoluminescence techniques to investigate film structures and luminescence properties. It was shown that more stronger C-H stretching and bending modes can be identified in FT-IR spectrum compared with the methane-based a-C:H. A intense band around 1450cm⁻¹ indicates that xylene-based a-C:H is polymer-like films containing high hydrogen concentration. In Raman spectrum, several peaks can be found, in which the peaks around 1445cm⁻¹, 2860cm⁻¹, 2925cm⁻¹ and 3057cm⁻¹ can be assigned to sp³ and sp² C-H vibration modes. It is interesting to see that a peak around 1600cm⁻¹ contains two bands, one is related to the G-peak (graphite) and another can be attributed to the existence of the aromatic structures. Photoluminescence (PL) was measured by using Xe lamp as excitation light with wavelength of 350nm and two peaks can be observed at room temperature, which is centered at 415nm and 475nm, respectively. With changing the wavelength of excitation light, the PL peak is not shifted but the relative intensity is changed. The origin of blue light emission from present a-C:H films is discussed in this paper. This work is supported by NSF of China (Grant No. 59802004) and Keli/Huake fellowship.

U7.21

STRUCTURAL AND MECHANICAL PROPERTIES OF DLC FILMS PREPARED BY PLD WITH VARYING LASER INTENSITY. M. Bonelli, A. Miotello, INFN-Dipartimento di Fisica, Università di Trento ITALY; P.M.Ossi, INFN-Dipartimento di Ingegneria Nucleare, Politecnico di Milano, ITALY.

Pulsed laser deposition (PLD) has the unique characteristic to allow for synthesizing at ambient temperature hydrogen free amorphous carbon films with a high content of sp³ hybridized material. The structure and properties of such DLC films strongly depend on deposition parameters, in particular the laser intensity. In the case of KrF excimer lasers, a threshold value of 3 × 10⁸ Wcm⁻² has been

reported for the attainment of carbon films with DLC properties. In this work DLC films, with thickness between 120 nm and 760 nm have been deposited at room temperature by ablation of a HOPG target, using a KrF excimer laser at intensities ranging from 2.5 × 10⁷ to 1.5 × 10⁹ W cm⁻². (100)Si substrates were used, and the role of interlayers such as SiC, TiC and TiN, with typical thickness of 500 nm, to improve film adhesion and mechanical properties was studied. IR spectra confirmed that the films are hydrogen free; their structure was studied by Raman spectroscopy, both in the visible (514.5 nm Ar line) and in the UV (244 nm Ar line) and by EELS; the fraction of sp³ hybridized carbon increases with pulse intensity and ranges between 42% and 80%. Film hardness, as measured by nanoindentation at 50 nm indentation depth, increases with sp³ content from 26 to 40 GPa in films deposited on (100)Si; the presence of a SiC interlayer brings film hardness up to 70 GPa and Young's modulus up to about 550 GPa. Scratch tests were performed with a Revetest Scratch-Tester using a diamond indenter with hemispherical tip, with a radius of 100 microns. The critical load at which adhesion fails increases with pulse intensity from 4 N to 18 N and concurrently the friction coefficient decreases from 0.1 to 0.05. In conclusion DLC films have been obtained by PLD even at pulse intensities so low as 2.5 × 10⁷ W cm⁻²; film mechanical properties have been tested both by nanoindentation and by scratch tests.

U7.22

INTERACTION OF OXYGEN WITH NANOPHASE CARBONS INVESTIGATED BY ELECTRON SPIN RESONANCE SPECTROSCOPY. A. Manivannan and M.S. Seehra, Physics Department, West Virginia University, Morgantown, WV.

Interaction of oxygen with three commercial carbons (GX203, P1400 and Med50 supplied by PICA USA Inc. with BET surfaces areas of 1000, 1150 and 2000 m²/g respectively) is reported using 9 GHz electron spin resonance (ESR) spectroscopy. X-ray diffraction and Raman spectroscopy of these carbons show them to contain graphitic crystallites with L_a ≈ 30 Å and L_c ≈ 10 Å [1]. ESR spectroscopy of these carbons yield a single line with g = 2.0028 (3). However, the ESR linewidth ΔH and integrated intensity I are found to be very sensitive to air/oxygen. For the evacuated samples, ΔH is reduced to 1.2 Oe from ΔH ≈ 4 Oe for the unevacuated samples. The intensities I of the lines are enhanced upon evacuation by factors of 40, 130, and 670 for GX203, P1400 and Med50 carbons respectively, correlating well with their specific surface areas. It is proposed that the ESR signal is due to uncompensated surface dangling bonds, the measured density of which is ≈ 10¹⁹/g. This concentration yields a calculated dipolar ΔH ≈ 1 Oe, in agreement with the experiment. Further, the dangling bonds interact with the spins of adsorbed oxygen molecules, broadening the line and reducing its intensity. The correlation with the surface area noted above then follows. Results on the variation of the ESR parameters of the ESR line with temperature and oxygen partial pressures will be presented. [1]. A. Manivannan, M. Chirila, N.C. Giles and M.S. Seehra, Carbon (in press).

U7.23

CARBON BLACK AGGLOMERATION IN POLYETHYLENE: THE PERCOLATION TIME PHENOMENON. Vaclav Bouda, Jiri Chladek, Jiri Rajman, Czech Technical University, Dept of Electrical Engineering, Prague, CZECH REPUBLIC.

In polymer compounds with carbon black (CB) content, the CB-volume fraction at which a CB-network of touching CB-particles (percolation threshold) is formed is not a constant but depends on the manufacturing process. It was found that the resistivity of a plastic that has a lower CB-concentration than the percolation threshold shows a percolation-like transition. This can be observed when the samples are held at a temperature higher than the glass transition temperature T_g or melt temperature T_m of the polymer matrix for a certain period or percolation time. At this characteristic time, a sharp step decrease in resistivity occurs. It is shown that by applying the theory of colloids, the results of the experimentally found percolation times can be explained. The coulombic force can cause a potential energy barrier to hinder the CB-particles from coming into close enough contact with each other to form a conductive carbon network. The barrier can be surmounted either by external shear forces or by reduction of the repulsive coulombic force by increasing the ionic concentration. The critical ionic concentration can be reached either above a critical salt concentration or after a certain time (percolation time) of special heat treatment of the composite melt in electrical field. The internal structure of the interlayers between the CB-aggregates and of the internal structure of the individual CB-aggregates become similar, i.e., the paracrystalline layers of CB-aggregates can extend from one aggregate into the next.

U7.24

VOIDS INVESTIGATION IN AMORPHOUS CARBON FILMS DEPOSITED BY dc-MAGNETRON SPUTTERING: A SMALL ANGLE X-RAY SCATTERING AND GAS THERMAL EFFUSION STUDY.

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Amorphous carbon films were deposited onto Si, Kapton and Al foils by dc-magnetron sputtering with different Ar plasma pressures, from 0.17 to 1.4 Pa, leading to films with different structural arrangements. The structure of these films evolve from a diamond-like film to a polymer-like one with increasing deposition plasma pressures, as revealed by Raman and optical characterization [1]. In this work, we investigate the voids structure and void density in these films by means of small angle x-ray scattering (SAXS) and mass spectrometry of gases effused from the films. The SAXS measurements were carried out at the National Synchrotron Light Laboratory at Campinas, Brazil, with a monochromatic x-ray beam of 1.608 Å. For the gas evolution measurements, films deposited onto Si substrate were inserted in a quartz tube evacuated by a turbomolecular pump and heated up to 1000°C, at a heating rate of 20°C/minute. The partial pressures of fragments with mass 2 and 13-18 were monitored with a quadrupole mass analyzer. The analysis of the effusion spectra provided clear evidence that films deposited at lower pressures are compact, while the films deposited at higher pressure present a more open structural arrangement. SAXS results confirm that the fraction of open volumes increases with the plasma pressure. On the other hand, through Guinier plots, a wide distribution of void sizes could be inferred. The results are discussed on the light of density measurements by using ion beam techniques, that indicates an increase from 1 to 1.4×10^{23} atoms/cm³ in the film density for the Ar pressure range here studied. [1] L.G. Jacobsohn and F.L. Freire Jr., J Vac. Sci. Technol. A, 17 sep/oct (1999)-in press.

U7.25

LOCAL STRUCTURE OF NANOPOROUS CARBONS. V. Petkov, R.G. DiFrancesco and S.J.L. Billinge, Michigan State University, Dept. of Physics and Astronomy and Center for Fundamental Materials Research, East Lansing, MI; M. Acharya and H.C. Foley, Center for Catalytic Science and Technology, Dept. of Chemical Engineering, University of Delaware, Newark, DE.

The local structure of nanoporous carbons produced by pyrolysis of poly(furfuryl alcohol) at various temperatures has been studied using neutron diffraction. Atomic pair distribution functions (PDFs) were obtained from the powder data. Structure models have been fit to the PDFs to understand the fine features of the atomic ordering. It has been found that carbons produced at 800°C and 1200°C are made of stacked graphene sheets, that are more or less curved. The 400°C processed carbon has a heavily distorted, non-planar structure. For each sample we have determined the extent of structural coherence, the average density within the structurally coherent regions and the proportion of carbon atoms, which are trigonally coordinated. We have also produced microscopic models for the local structure of the nanoporous carbons investigated.

U7.26

NOVEL SILICA SOL MEDIATED SYNTHESIS OF NANOPOROUS CARBONS WITH REGULAR PORES. Taeghwan Hyeon, Sangjin Han, School of Chemical Engineering, Seoul National University, Seoul, KOREA.

We will present a new synthetic methodology to produce nanoporous carbons with regular pore size distributions. Commercially available Ludox silica sols have been utilized as template for the synthesis of nanoporous carbons. Resorcinol and formaldehyde (RF) were polymerized in the presence of inorganic silica sol particles to generate silica-RF composites. Pyrolysis followed by the HF etching of the composites produced porous carbons. Pore size distribution revealed that the pores of the carbon ranges in size from 40 nm to 80 nm. The surface area of the carbon was found to be 1227 m²/g. Pore volume was as high as 1.6 cm³/g. When silica sol particles stabilized with surfactants were applied as templates, nanoporous carbon with remarkably narrow pore size distribution of 8 nm has been generated. This carbon material has a surface area of 1090 m²/g and pore volume of 1.7 cm³/g. In this presentation the synthesis, characterization and electrochemical properties of these nanoporous carbon materials will be discussed.

U7.27

SURFACE CHARACTERIZATION OF NANOSTRUCTURED CARBON FILMS GROWN BY CLUSTER BEAM DEPOSITION. Matteo Bogana, Davide Donadio, Luciano Colombo, Giorgio Benedek, INFN and Dept. Materials Science University of Milan Bicocca, Milano, ITALY; Paolo Milani, INFN and Dept. Physics, University of Milano, Milano, ITALY.

We present a theoretical investigation on fractal properties of nanocrystalline films obtained by supersonic beam deposition of

carbon clusters. By analogy with experimental STM and AFM investigations, we adopted a surface definition based on an AFM-like concept, using tips of different curvature in order to investigate the morphology of the surface structure. The computed height-height correlation function shows that correlation length and self affinity are strongly related to system relaxation during deposition. For thermalized structures we calculated the scaling behavior, finding an excellent agreement with experimental data [2]. This work has been performed within the PRA-CLASS project. [1] D. Donadio, L. Colombo, P. Milani, G. Benedek, in press (1999). [2] P. Milani, to be published.

SESSION U8: POSTER SESSION: DIAMOND, SiC, AND RELATED MATERIALS

Chairs: Tatiana Allen and Otto Zhou

Tuesday Evening, November 30, 1999

8:00 P.M.

Exhibition Hall D (H)

U8.1

NANOCRYSTALLINE SILICON CARBIDE FILM GROWTH USING HOT FILAMENT CVD. M.B. Yu, Rusli, S.F. Yoon, J. Cui, J. Ahn, Q.Zhang, Nanyang Technological University, School of Electrical and Electronic Engineering, SINGAPORE.

Silicon carbide (SiC) is one of the wide gap semiconductors and has been studied for blue light emitting diode (LED). However, due to its indirect gap, the quantum efficiency of the LED is very low. Therefore, enhancement of the luminescence intensity is strongly desired. Attention on Si base emission materials has switched to using quantum confinement effect of nanocrystalline Si grain embedded in a matrix of Si nitride or oxide that could result in strong visible light emission. If nanocrystalline SiC films could be similarly fabricated, it is possible to obtain high efficiency short wavelength emission. Towards this objective, we have investigated the growth of nanocrystalline SiC films using the hot filament chemical vapour deposition (HFCVD) technique. The samples were deposited in an ultra-high vacuum HFCVD equipment. By using a suitable deposition technique, SiC films embedded with smaller grain crystals were obtained. From the high resolution TEM picture, nanometer crystalline grains can be clearly seen. Photoluminescence of the sample revealed a visible peak at 2.2 eV. X-ray photoelectron spectroscopy (XPS) measurements showed that the atomic percentages of Si and C are nearly 50%. The x-ray diffraction spectrum of the sample revealed a diffraction peak of 3C-SiC (111) at $2\theta=35.6^\circ$. The FWHM of this peak is 1.5° , which according to Debye-Scherrer's formula, indicates an average grain size of about 7.2 nm. Fourier transform infrared absorption spectrum of the film revealed an obvious absorption peak at 800 cm^{-1} which is related to the TO phonons of Si-C bonds in 3C-SiC. Raman spectrum of the sample showed that there are two peaks at 790 cm^{-1} and 970 cm^{-1} which corresponded to longitudinal and transverse optical phonons of SiC respectively. In summary, nanocrystalline SiC films were fabricated using the HFCVD method and visible light photoluminescence was obtained at room temperature. Structural characterizations have demonstrated the successful fabrication of SiC nanocrystallites in an amorphous SiC matrix.

U8.2

AMORPHOUS CARBON-SILICON ALLOYS PREPARED BY A HIGH PLASMA DENSITY SOURCE. A.C. Ferrari, N.A. Morrison, W.I. Milne, J. Robertson, Engineering Department, Cambridge University, Cambridge, UNITED KINGDOM.

The addition of silicon to hydrogenated amorphous carbon can have the advantageous effect of lowering the compressive stress, improving the thermal stability of its hydrogen and maintaining a low friction coefficient up to high humidities. Most experiments to date have been on a-C_{1-x}Si_x:H alloys deposited by RF plasma enhanced chemical vapour deposition. This method leaves gives alloys with considerable hydrogen content and only moderate hardness. Here, we use a high plasma density source, the electron cyclotron wave resonance (ECWR) source, to prepare films of lower H content to increase the hardness, while controlling the ion energy so as not to increase the stress. The composition and bonding in the alloys is determined by Rutherford Backscattering, visible and UV Raman and IR. We find that it is possible to increase the sp³ content without increasing the stress. The band gap however is found to remain below 2.5 eV.

U8.3

EFFECT OF HYDROGEN DILUTION ON OPTICAL PROPERTIES OF a-Si_{1-x}C_xH PRODUCED WITH TETRAMETHYLSILANE. M. Park, V. Sakhrani, C.W. Teng¹, D.J. Kim, S.-H. Kim, R.M. Kolbas¹, R.J. Nemanich², R.C. Sanwald and J.J. Cuomo, Dept. of Materials Sci. and Eng, North Carolina State

Univ., Raleigh, NC; ¹Dept. of Electrical and Com. Eng., North Carolina State Univ., Raleigh, NC; ²Dept. of Physics, North Carolina State Univ., Raleigh, NC.

Thin films of wide bandgap amorphous semiconductor (a-Si:C:H) were prepared by the decomposition of tetramethylsilane in a 13.56 MHz radio-frequency glow discharge. The films were deposited on single crystal silicon, glass, and sapphire substrates. Bonding configuration of the films was studied by micro-Raman spectroscopy and FT-IR spectroscopy, vis-a-vis nuclear magnetic resonance spectroscopy. X-ray photoelectron spectroscopy, optical absorption, and spectroscopic ellipsometry were also used for materials characterization. A very broad photoluminescence peak at ~ 450 nm (FWHM ≈ 1600 nm) was observed at room temperature with UV excitation. Increasing hydrogen dilution during deposition dramatically shifted the optical absorption edge to higher energies and altered the relative emission intensity within the broad emission peak. The optical bandgap, determined from Tauc plots, increased dramatically upon hydrogen addition. The effects of the addition of hydrogen on the optical properties will be discussed.

U8.4
EFFECTS OF COMPOSITION ON THE MICROSTRUCTURES AND OPTICAL PROPERTIES OF HYDROGENATED AMORPHOUS SILICON CARBIDE FILMS PREPARED BY ELECTRON CYCLOTRON RESONANCE PLASMA CHEMICAL VAPOR DEPOSITION. Lih-Hsiung Chan, Wei-Zen Chou¹, and Lih-Hsin Chou, National Tsing Hua Univ., Dept. of Materials Science and Engineering, Hsinchu, TAIWAN, R.O.C.; ¹present address: TSMC, Hsinchu, TAIWAN, R.O.C.

Hydrogenated amorphous silicon carbide films (a-SiC:H) were prepared from CH₄, SiH₄, and Ar mixtures by Electron Cyclotron Resonance Plasma Chemical Vapor Deposition. The thin films were deposited under the optimized conditions, microwave power : 900W, and Ar flux: 90scm. The uncooled substrate temperature was around 100-120°C during deposition. The relative flux ratio of methane to silane was varied to produce thin films of different compositions to investigate the relationship between the compositions of films and the associated microstructures and optical properties. Furthermore, how the optical properties were related to the microstructures was analyzed. The surface morphology and amorphous microstructures were confirmed by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM), respectively. X-ray Photoelectron Spectroscopy (XPS) was employed to study the relative atomic ratio of C to Si, and bonding conditions in the thin films. The hydrogen concentration and the amounts of C-H and Si-H bonds were determined by Fourier Transform Infrared Spectroscopy (FTIR), while the optical properties were measured by optical spectrophotometer.

U8.5
MECHANICAL AND ELECTRICAL PROPERTIES OF CSi_xN_y, CB_xN_y, CN_x AND DLC THIN FILMS GROWN BY N-PLASMA ASSISTED PULSED LASER DEPOSITION. Thomas Thärigen, Volker Riede and Michael Lorenz, University of Leipzig, Faculty of Physics and Earth Sciences, Leipzig, GERMANY; Eberhard Hartmann, Gerd Lippold, Institute for Surface Modification, Leipzig, GERMANY; Ronald Hesse, Peter Streubel, University of Leipzig, Faculty of Chemistry and Mineralogy, Leipzig, GERMANY; Dirk Lorenz, Peter Grau, Martin-Luther-University Halle-Wittenberg, Department of Physics, Halle/Saale, GERMANY.

Carbon silicon nitride (CSi_xN_y), carbon boron nitride (CB_xN_y), carbon nitride (CN_x) and diamondlike carbon (DLC) thin films have been grown by pulsed laser deposition (PLD) of various carbon (silicon/boron) (nitride) targets using an additional nitrogen RF plasma source on (100) oriented silicon substrates without additional heating. The CSi_xN_y and CB_xN_y thin films were amorphous and showed nanohardness up to 23 GPa compared to 14 GPa for silicon, maximum nitrogen content of 30 at%, and maximum silicon content up to 20 at%. The maximum nanohardness was achieved for 5 at% Si or B content in the films. The lower hardness of these films compared to the nanohardness of 71 GPa of the DLC films indicates a low amount of covalent carbon-nitrogen bonding in the films. However, in contrast to DLC films, the CSi_xN_y and CB_xN_y films can be grown to thickness above 1 μm because of much lower internal stress. Increasing carbon double and triple bonding of the CSi_xN_y and CB_xN_y films in dependence on the deposition process as identified by FTIR and Raman spectroscopy correlates to decreasing nanohardness. XPS of CSi_xN_y and CB_xN_y film surfaces shows clear correlation of binding energy and intensity of N 1s, C 1s, and Si 2p peaks to composition of the targets and to nitrogen flow through plasma source, indicating soft changes of binding structure due to variation of PLD parameters. Electron cold emission from residues layers of detached DLC thin films showed extremely low field thresholds of 18.6 kV/cm up to emission currents of 0.5 mA. The results demonstrate the capability of the plasma assisted PLD process to deposit hard amorphous CSi_xN_y,

CB_xN_y, CN_x and DLC thin films with variable properties. This work is supported by the German Research Community DFG under Grant No. INK24.

U8.6
THE CHEMICAL BONDING AND CRYSTALLINE STATE OF HARD BORON-BASED COATINGS. Alan Jankowski, Lawrence Livermore National Laboratory, Livermore, CA.

Boron coatings are deposited by sputtering fully dense, pure Boron targets using planar magnetrons operated in the rf mode. Boron-alloy coatings are formed by sputtering compound targets, through co-deposition with other elemental targets, by utilizing reactive gas mixtures as Argon-Nitrogen, and/or by post-deposition implantation. Transmission electron microscopy, bright field imaging and selected area diffraction are used to reveal texturing in crystalline phases through the formation of amorphous phases in the Boron-based coatings. The phase formed is found to be dependent on both coating composition and the sputter deposition conditions. Near-edge x-ray absorption fine structure analysis reveals features of chemical bonding in the Boron 1s photoabsorption spectrum that can be correlated with the crystalline state and surface hardness as measured using nanoindentation. Amorphous Boron-based coatings can be formed with hardness values approaching 80% of cubic Boron-Nitride. This work was performed under the auspices of the United States Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

U8.7
COMPUTATIONAL CHEMISTRY STUDY ON DYNAMIC BEHAVIOR OF GROWTH SPECIES OF DIAMOND ON SUBSTRATES. Seiichi Takami, Hui Zhou, Hiroyuki Tamura, Momoji Kubo, Akira Miyamoto, Tohoku Univ., Dept. of Materials Chemistry, Sendai, JAPAN; Akira Imamura, Hiroshima Kokusai Gakuin Univ., Dept. of Mathematics, Hiroshima, JAPAN.

We have developed a molecular dynamics simulation code to study chemical reactions of radicals. This code employed a modified extended Hückel approximation to consider the spin states as well as the electronic behavior of system. Dynamics of growth species including CH₃, H, C₂H with various velocities during and after their collision with diamond surfaces were simulated. Diamond surfaces were represented by model clusters whose typical size was C₃₈H₄₂. Experimental results by other researchers indicated that the quality of obtained diamond or diamond like carbon films depended largely on experimental conditions, implying that the population of growth radical species predominantly determined the film quality. We present the results of our investigations and discuss the implications of our finding as a guideline to obtain films with desired qualities.

U8.8
AN AUGER AND XPS STUDY OF DIAMOND SURFACES. Jane Y. Howe, Linda E. Jones, New York State College of Ceramics at Alfred University, Alfred, NY; David N. Braski, The High Temperature Materials Laboratory, Oak Ridge National Laboratory, Oak Ridge, TN.

There is an interest in the oxidation behavior of diamond surface because the development and application of diamond based electronic devices. CVD diamond films manufactured by Norton Diamond Film, Inc. and Type 2A natural diamonds with specific exposed facets, i.e., {111}, {110}, and {100}, are the subjects of the current research effort. HOPG graphite and glassy carbon are the reference materials. Preliminary experiments were conducted to determine if the ET100 films could be analyzed by Auger electron spectroscopy or whether electron charging would be too severe to permit such an analysis. The as-grown side of the film was analyzed using PHI 660 Scanning Auger Microprobe with an accelerating voltage of 2 kV. The spectra were collected at (a) as-received, (b) after 10 s sputtering with Ar ions, and (c) after 60 s sputtering conditions. Charging was observed when analyzing the as-received film. It increased as the partially-conducting surface contamination was removed by ion sputtering. The sputtering rate was estimated to be approximately 200 Å/min. However, charging was restricted to low energies and the spectra above 100 eV were intact and peak shapes remain unchanged. These results indicated that the impurity elements can be identified, concentrations estimated, and peak shape resolved in order to identify different structure types, e.g., diamond v.s. amorphous carbon, v.s. graphite, and etc. Oxidation state information of these materials is, however, difficult to acquire. Gross effects of charging on peak shift tend to mask any subtle peak-shifts due to changes in oxidation state. Such changes in oxidation state are better studied using XPS where X-Rays are used instead of electrons to generate the spectra. This paper addresses the use of Auger and XPS in the study of diamond surface modification by oxygen.

U8.9

PERIODIC DENSITY FUNCTIONAL STUDY ON OXIDATION OF DIAMOND (100) SURFACES. Hiroyuki Tamura, Hui Zhou, Yoshihisa Hirano, Seiichi Takami, Momoji Kubo, Akira Miyamoto, Tohoku Univ, Graduate School of Engineering, Dept of Materials Chemistry, Sendai, JAPAN; Akira Imamura, Hiroshima Kokusai Gakuin Univ, Dept of Chemical Engineering, Aki-ku Nakano, Hiroshima City, JAPAN; Mikka N. Gamo, Toshihiro Ando, Core Research for Evolutional Science and Technology (CREST), c/o National Institute for Research in Inorganic Materials (NIRIM), Tsukuba, Ibaraki, JAPAN.

The chemical reactions of the diamond surfaces with hydrogen and oxygen play important roles in the CVD process, etching and wear of the surface. Although many experimental measurements[1,2] and theoretical studies have been performed, the structure and energetics of the hydrogenated and oxygenated diamond surfaces are still unclear. In particular, there is only a handful theoretical studies for the oxygenated diamond surfaces in spite of their importance[3]. In the present study, the periodic density functional calculations have been performed to clarify the oxidation mechanisms of the hydrogenated diamond (100) surfaces. The reaction paths of the oxidation have been simulated in terms of the reaction heats. The ether, hydroxyl and ketone structures are found to be stable on the diamond (100) surfaces. At the initial stage of the oxidation, the ether structures are priority formed at monohydride dimer bonds on the diamond (100) surfaces. The oxidations into the lower layer of the diamond crystal are much endothermic. As the coverage of oxygen atoms on the diamond surface is increased, the formation of ketone structures becomes easier. [1] T. Ando, M. Ishii, M. Kamo, Y. Sato, J. Chem. Soc. Faraday Trans. 89, 1783 (1993). [2] T. Ando, K. Yamamoto, M. Ishii, M. Kamo, Y. Sato, J. Chem. Soc. Faraday Trans. 89, 3635 (1993). [3] S. Skokov, B. Weiner, M. Frenklach, Phys. Rev. B 49, 11374 (1994).; Phys. Rev. B 55, 1895 (1997).

U8.10

ALTERING RESISTIVITY IN DIAMOND FILMS WITHOUT IMPURITY ADDITION. Karen M. McNamara, Colin Baker, Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, MA.

Resistivity of semiconductors is usually controlled by impurity addition. For example, CVD diamond is often doped with boron. In the case of diamond, however, there is a second mechanism for altering resistivity as a result of carbon's ability to form sp^2 hybridized bonds. In this work, we have used gas phase chemistry to control the incorporation of sp^2 hybridized carbon during diamond growth. While the bulk structure of the material is that of diamond, small amounts of sp^2 carbon can alter the resistivity dramatically. We have observed variations over 10 orders of magnitude. To gain insight into the mechanism of conduction within the materials, temperature dependent resistivity measurements were carried out. These results, combined with Raman spectroscopy, growth studies and microscopic analysis, allow us to differentiate conduction mechanisms in the film. The application of these materials will also be briefly discussed.

U8.11

THE ELECTRONIC STRUCTURE OF HEAVY METAL IMPURITIES IN DIAMOND. Richard J. Anderson, Sandia National Laboratories, Livermore, CA.

We present the time-resolved photoluminescence spectroscopy, photoluminescence excitation spectroscopy, and photocurrent spectroscopy of diamond into which tantalum, tungsten, rhenium, and osmium have been incorporated during growth. The data indicate that the heavy metal impurity symmetrically occupies the divacancy site in the diamond lattice. We infer also that the highest lying occupied electronic level of each successively heavier 5d impurity approaches more closely the conduction band

U8.12

MOLECULAR DYNAMICS SIMULATION OF SI IMPURITIES IN NANOCRYSTALLINE DIAMOND GRAIN BOUNDARIES. Peter Zapol, Larry A. Curtiss, Dieter M. Gruen, Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL; Michael Sternberg, Thomas Frauenheim, Department of Physics, University of Paderborn, Paderborn, GERMANY.

Nanocrystalline diamond films grown on Si substrates at 800°C from hydrogen-poor plasmas have a number of highly desirable mechanical and electronic properties. Si was found by SIMS measurements to be uniformly distributed throughout the thickness of the films at a level of 10^{17} - 10^{18} cm⁻³. It is likely that the Si is located at the grain boundaries, which play a crucial role in controlling important characteristics of the films, such as electrical conductivity and electron emission. Density-functional based tight-binding (DFTB) molecular dynamics simulations were performed for diamond high-energy high-angle (100) twist grain boundaries. The method was

successfully applied before to study carbon systems and carbon/silicon interfaces. Twist grain boundaries in diamond have recently been shown by other workers to have a large fraction of three-coordinated carbon atoms in sp^2 configuration. We have found that average coordination number of carbon atoms is locally higher in the vicinity of a Si impurity in the grain boundary region. Electronic and vibrational properties of grain boundaries with Si were obtained. Electronic levels associated with Si atoms are located in the band gap of diamond. The electron density distribution around Si is discussed. (Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.)

U8.13

UV RAMAN STUDIES OF MICROCRYSTALLINE DIAMOND. Katsuyuki Okada, Hisao Kanda, Shojiro Komatsu, and Seichiro Matsumoto, National Institute for Research in Inorganic Materials, Tsukuba, JAPAN.

Microcrystalline diamond films have been prepared in a 13.56 MHz low pressure inductively coupled plasma.¹ The pressure of CH₄/H₂ and/or CH₄/CO/H₂ plasma was varied from 45 to 50 mTorr. The substrate temperature was kept at 900°C. The obtained deposits were analyzed by using Raman spectroscopy with visible 514 nm excitation and ultraviolet 325 nm and 244 nm excitation. 514 nm excited Raman spectra exhibit two broad Raman peaks at ~1355 cm⁻¹ and ~1580 cm⁻¹ corresponding to sp^2 bonding without CO additive (CH₄/H₂ plasma). New peaks at ~1150 cm⁻¹ assigned to sp^3 bonding and at ~1480 cm⁻¹ appear with CO additive (CH₄/CO/H₂ plasma); the two peaks due to the sp^2 bonding disappear with increasing CO additive. 325 nm excited Raman spectra show a shoulder at ~1150 cm⁻¹, and peaks at 1333 cm⁻¹ due to sp^3 bonding and at ~1580 cm⁻¹ are remarkably enhanced. In 244 nm excited Raman spectra, the peak at 1333 cm⁻¹ is only enhanced whereas the peak at ~1580 cm⁻¹ is weakened. The visible 514 nm excited Raman spectra imply that the vibrational modes of sp^2 sites are resonantly enhanced because the 514 nm (2.4 eV) corresponds to the π - π^* transition at sp^2 sites. On the other hand, the ultraviolet 325 nm (3.8 eV) and 244 nm (5.1 eV) excited Raman spectra reveal that the UV excitation is sufficient to excite the σ state of both sp^2 and sp^3 sites. 1) K. Okada, S. Komatsu, and S. Matsumoto, J. Mater. Res., 14, 578(1999).

SESSION U9: APPLICATIONS OF AMORPHOUS AND NANOSTRUCTURED CARBON – ELECTRICAL, CHEMICAL, AND MECHANICAL
Chairs: Paolo Milani and John P. Sullivan
Wednesday Morning, December 1, 1999
Room 311 (H)

8:30 AM *U9.1

SYNTHESIS AND CHARACTERIZATION OF CLUSTER-ASSEMBLED CARBON FILMS. P. Milani, E. Barborini, P. Piseri, INFN-Dipartimento di Fisica, Università di Milano, Milano, ITALY.

Here we will present and discuss the use of supersonic cluster beam deposition for the production of nanostructured carbon thin films. With this technique nanostructured films can be produced over large areas on various substrates at room temperature. Elemental building blocks are clusters with a number of atoms ranging from few tens up to few hundreds. These units organize in the film in hierarchical structures from the nanoscale to the mesoscale. By separation effects typical of supersonic beams it is possible to select different mass distributions of neutral clusters in the beam, allowing the deposition of thin films with controlled nanostructure. SEM, AFM, Raman and electronic spectroscopy show that the films are low-density porous networks with sp^2 and sp bondings, whose ratio depends on the precursors clusters, confirming the existence of a memory effect. Structural and functional properties of cluster-assembled carbon have been characterized showing that this is a form of partially disordered carbon different from other amorphous carbons. The structure of cluster-assembled carbon makes this material particularly promising for applications such as field emission and energy storage. In particular the realization of supercapacitors based on cluster-assembled carbon films will be presented.

9:00 AM U9.2

HYDROGEN STORAGE IN CARBON BASED MATERIALS. Ping Chen, Gang Chen, Jianyi Lin, Kuang Lee Tan, National University of Singapore, Physics Department, Singapore, SINGAPORE.

Alkali metal-modified carbon materials, including carbon nanotubes, carbon nanofibers, activated carbon, graphite etc., can be applied as high efficient hydrogen storage media (up to 14 wt% of hydrogen can be absorbed at moderate temperature). The hydrogen storage

capacity as well as storage conditions are affected by the structure of carbon materials which was further investigated by the in situ FTIR, TGA, XRD, XPS etc. techniques.

9:15 AM U9.3

ELECTROCHEMICAL STORAGE OF LITHIUM IN SINGLE WALL CARBON NANOTUBES. Agnes Claye, John E. Fischer, University of Pennsylvania, Dept. of Materials Science and Engineering, Philadelphia, PA.

Since their discovery in 1991, single wall carbon nanotubes (SWNT) have generated considerable interest due to their novel electronic properties and their expected high tensile strength. Potential applications for this new form of nanostructured carbon include nanoscale electronic devices, fillers for nanocomposites, field emitters, and energy storage.

We investigated the potential use of SWNT as an anode in rechargeable lithium ion batteries. We will report on the properties of SWNT upon electrochemical doping with lithium. Results from galvanostatic charge-discharge, cyclic voltammetry, and electrochemical impedance spectroscopy will be presented. The electrochemical performance of SWNT in different electrolyte systems will be compared. The effect of electrochemical doping on the structural and electronic properties of SWNT will be discussed, offering some clues about the lithium insertion mechanism.

9:30 AM U9.4

ELECTRONIC PROPERTIES OF POTASSIUM-DOPED CARBON NANOTUBE LATTICE. Susumu Saito, Department of Physics, Tokyo Institute of Technology, Tokyo, JAPAN.

Carbon nanotubes were theoretically predicted to possess and have been actually confirmed experimentally to have topology-dependent electronic properties. They are therefore now being studied intensively from the viewpoint of the material for nanoelectronics in the next century. The nanotube network consists of hexagons as in the case of graphite. Hence the carrier doping via intercalation is attracting strong interests. I report the electronic properties of the K-doped crystalline lattice of so-called (10,10) nanotubes obtained by using the density-functional theory treatments. The stoichiometry of the system studied is $(K_2C_{40})_2$ which can be realized without expanding the intertube spacing. The electronic band structure will be compared to that of the undoped material, and the carrier distribution will be discussed in detail.

9:45 AM U9.5

GROWTH OF HIGH RESOLUTION CARBON NANOTUBE SCANNING PROBE MICROSCOPY TIPS BY CHEMICAL VAPOR DEPOSITION. Jason H. Hafner, Chin Li Cheung, Charles M. Lieber, Harvard Univ, Dept of Chemistry and Chemical Biology, Cambridge, MA.

Carbon nanotubes are ideal probes for atomic force microscopy (AFM) due to their nanometer-scale diameter, high aspect ratio, and superior mechanical properties. Covalent modification of the ends of nanotubes with organic and biological species also enables functional imaging and binding studies at the single molecule level. Carbon nanotube AFM tips have previously been produced by mechanical assembly from pre-formed nanotube material. However, this technique is time consuming and selects towards thicker bundles of nanotubes. Herein we describe a chemical vapor deposition (CVD) approach for the growth of nanotubes from commercial silicon tips. The CVD approach is a straight-forward means of fabricating nanotube AFM tips, and it can potentially be scaled up for commercial production. Our CVD growth approach provides individual nanotube tips, rather than bundles, and thus offers substantial improvements in resolution. Mechanical measurements made on the CVD nanotube tips demonstrate that CVD nanotube tips elastically buckle rather than break when large normal forces are applied, thus making them highly robust. Ultimately, the CVD technique should enable the production of individual single-walled nanotube tips that could achieve unprecedented resolution with a ca. 0.5 nanometer end radius of curvature. The application of CVD nanotube tips to high-resolution AFM imaging of isolated biomolecules and progress towards the growth of single-walled nanotube tips will be discussed.

10:30 AM U9.6

CARBON NANOTUBE COMPOSITES - STRONGEST ENGINEERING MATERIAL EVER? Bradley S. Files, Brian Mayeaux, Pavel Nikolaev, William Profft, NASA-Johnson Space Center, Materials, Manufacturing and Process Technology Division, Houston, TX.

The primary goal of the carbon nanotube project at Johnson Space Center (JSC) is to fabricate structural materials with a much higher strength-to-weight ratio than any engineered material today. Single-wall nanotubes present extraordinary mechanical properties

along with new challenges for materials processing. Also, interesting anisotropic thermal and electrical properties could lead to multifunctional and hierarchical materials. Our project includes nanotube production, characterization, purification, and incorporation into applications studies. NASA has included the pursuit of breakthrough technologies as part of its plan to expand human exploration of the solar system. Now is the time to move from studying individual nanotubes to applications work. Current research at JSC focuses on structural polymeric composites to attempt to lower the weight of spacecraft necessary for interplanetary missions. These nanoscale fibers present unique new challenges and processing concerns to composites engineers. Preliminary studies show good nanotube dispersion and wetting by the epoxy resin. Results of tensile strength tests will also be reported. Other applications of nanotubes are of interest for energy storage, gas storage, nanoelectronics, field emission, and biomedical uses.

10:45 AM U9.7

THERMAL CONDUCTIVITY OF AMORPHOUS THIN FILMS. Andrew J. Bullen, David G. Cahill, University of Illinois, Urbana, IL; Othon Monteiro, Lawrence Berkeley National Laboratory, Berkeley, CA; Achim von Keudell, Max-Planck Institut für Plasmaphysik, Garching bei München, GERMANY.

Solid forms of carbon provide the largest (diamond) and nearly the smallest (amorphous C_{60} compacts) thermal conductivities known for fully dense materials at room temperature, suggesting that the atomic-scale microstructure of carbon thin films could lead to both high and low conductivity materials for thermal management applications. We have studied the thermal conductivities of a-C:H, and a-C films deposited by a variety of methods selected to span the range from low, polymer-like behavior to the relatively high thermal conductivities of "amorphous diamond". The through-thickness thermal conductivities are measured in the temperature range 80–400K using the 3ω method for thin films. We find that the density dependence of the data is in surprisingly good agreement with a simple effective medium calculation that models the density-deficits relative to diamond as atomic scale voids. The thermal conductivity of the extrapolated fully dense matrix is also in good agreement with the predicted "minimum thermal conductivity" for amorphous-diamond.

11:00 AM U9.8

HIGH REVERSE BREAKDOWN a-C:H/Si DIODES MANUFACTURED BY rf-PECVD. Shashi Paul, F.J. Clough, Emerging Technologies Research Centre, De Montfort University, Leicester, UNITED KINGDOM.

Thin films of hydrogenated amorphous carbon (a-C:H), deposited by radio frequency plasma enhanced chemical vapour deposition (rf-PECVD), have been studied for various applications. An interesting property of these films is their high breakdown strength (10^7 Vcm⁻¹). This property of a-C:H can be exploited in high breakdown heterostructure diodes or as a passivation and insulator layer in MIS devices. There are a number of reports on a-C:H/Si diodes for high voltage operation [1][2] but only one where the a-C:H films were deposited by rf-PECVD [3]. The diodes produced do not show reproducible I-V behaviour under high voltage stress. It was argued that trapped charges at the Al/a-C:H interface and in the bulk were responsible for the observed instability. Film quality is therefore an important consideration for the realisation of high voltage breakdown devices. We have investigated the process dependence of the structural and electrical properties of rf-PECVD a-C:H films to realise, for the first time, reproducible, high breakdown voltage diodes. Thin films of a-C:H were deposited at room temperature from a CH₄/Ar gas mixture (at a pressure of 100 mTorr) using a capacitively coupled rf-PECVD (13.56 MHz) system. Heterojunction diodes were manufactured by depositing the a-C:H on to a p-type Si substrate (200-220 Ωcm). Current-voltage (I-V) characteristics were measured using a pc-driven HP4140B picoammeter and a high voltage source HP4142B. Capacitance-voltage (C-V) measurements were made using an LCR bridge (HP4282A). Scanning Electron microscopy was also carried out to determine surface quality of the deposited films. We have observed a clear correlation between the dc self-bias and the rectification ratio of a-C:H/Si heterojunction diodes. Optimised diodes show rectification ratios up to 10^4 and a stable, reverse breakdown voltage typically around 850 V for a-C:H film thickness 200nm. I-V and C-V measurements show no evidence of hysteresis. The dependence of the reverse breakdown voltage on the a-C:H thickness will also be discussed in this report. References: [1] K. Knofoas, et al., J. Appl. Phys. 81 (1997) 6238 [2] S.B. Hwang, et al., Electronics Letts. 27 (1991) 2043 [3] G. Amaratunga et al., IEEE Elect. Dev. Letts. 11 (1990) 33

11:15 AM U9.9

DIAMOND LIKE CARBON COATINGS FOR RHENIUM STENTS. E.A. Evans, Univ. of Akron, Dept of Chemical Engineering, Akron, Ohio; U. Hafeli, Cleveland Clinic Foundation, Cleveland, OH.

Diamond like carbon has been deposited as a protective layer for coronary stenting applications. Taking advantage of DLC's stability, or resistance to chemical attack, its flexibility, and other properties, our current technical objective is to develop DLC as a coating for radioactive rhenium stents. Radioactive rhenium stents are being investigated to limit smooth muscle cell growth following coronary surgery. The DLC coating is being investigated to reduce the release of radioactive rhenium (free activity) into the blood following the stenting procedure. An inductively coupled RF plasma system was used to deposit the DLC onto rhenium substrates. Foils, wires, and coils were coated and tested for adhesion, cytotoxicity, and release of radioactive rhenium. Our initial results indicate a 50% decrease in the release of free activity relative to uncoated rhenium. Relationships between deposition parameters and DLC performance will be presented.

11:30 AM *U9.10

PATTERNING CARBONS USING SOFT LITHOGRAPHY.

George M. Whitesides, Harvard University, Dept of Chemistry and Chemical Biology, Cambridge, MA.

Soft lithography provides a flexible method of patterning a range of thermoplastic and thermoset polymers. When the polymers chosen are precursors to pyrolytic carbons, the combination of soft lithographic molding followed by pyrolysis provides a flexible method of generating micropatterned carbon structures. This talk will outline relevant methods of soft lithography, and describe types of carbon structures (and structures of other relevant materials) that can be made using these techniques.

SESSION U10/V7: JOINT SESSION: MECHANICAL PROPERTIES OF AMORPHOUS AND CRYSTALLINE CARBON

Chairs: John Robertson and Edward Shaffer II
Wednesday Afternoon, December 1, 1999
Room 311 (H)

1:30 PM *U10.1/V7.1

TRIBOCHEMISTRY OF ZDOL DECOMPOSITION WITH HYDROGENATED CARBON OVERCOATS. C. Singh Bhatia, IBM, San Jose, CA; Chao-Yuan Chen; Walton Fong; Changhong Jiang; David B. Bogy, University of California, Dept of Mechanical Engineering, Berkeley, CA; Simone Anders, Lawrence Berkeley National Laboratory, Berkeley, CA.

Tribo-chemical studies of the lubricant molecular weight effect on the tribology of the head/disk interface (HDI) were conducted using hydrogenated (CH_x) carbon disks coated with ZDOL lubricant. The studies involved drag tests with uncoated and carbon-coated Al_2O_3 -TiC sliders and thermal desorption experiments in an ultra-high vacuum (UHV) tribochamber. The studies showed that the lubricant interaction with the carbon overcoat varies as a function of lubricant molecular weight. The friction coefficient increases as the molecular weight increases. The higher friction is due to the higher viscosity. The friction and catalytic decomposition mechanisms of ZDOL are described. In general, the PFPE polymers are decomposed by chain scission involving the breakage of the backbone bonds to yield free-radical segments. Chain scission can occur by three mechanisms: (1) random degradation, (2) depolymerization, and (3) weak-link degradation. Our studies further support previous observations that catalytic reactions occurred at the endgroup functionals. The lower number of endgroup functionals for ZDOL with higher molecular weight reduces the possibility of the occurrence of catalytic reactions. Moreover, the ZDOL desorb peak temperatures shifted to lower temperatures with increasing molecular weight in thermal desorption tests. The spreading diffusion coefficient of ZDOL decreases with increasing molecular weight. As the mobility of the lubricant chain decreases, the desorption energy needed to break the lubricants increases, resulting in higher desorption peak temperatures. In addition, the longer chain length of the higher molecular weight ZDOL causes higher degrees of crosslinking. The crosslinking restricts chain mobility and causes an increase in the desorption peak temperatures. In summary, the talk will discuss the lube degradation due to tribo-chemical reactions at the head/disk interface.

2:00 PM U10.2/V7.2

IN-SITU WEAR MEASUREMENTS OF THIN CARBON FILMS. Vlad Novotny, TeraStor Corporation, San Jose, CA; Boris Druz, Veeco Instruments, Inc., Plainview, NY.

First optical surface recording heads and disks represent an ideal system to study tribology of thin films in-situ with a high degree of sensitivity. Quantitative measurements of wear of thin films usually involve an ex-situ evaluation of wear with mechanical profilometry,

atomic force microscopy, optical interferometry, ellipsometry or flying height interferometry. The optical beam that passes through the head can be used to monitor the head-disk spacing and, therefore, the wear of the thin film coated on the head surface. When the disk contains tracking grooves, diffraction of light from lands and grooves produces a tracking error signal, which depends on head-disk spacing. In addition, the light coupling between the head and disk optical surfaces generates an optical coupling signal that also depends on head-disk spacing. Moreover, an acoustic emission sensor produces a signal, which monitors physical contacts between asperities on the head and disk and effectively measures physical head-disk spacing. Head-disk spacing is adjusted externally, and tracking, coupling and acoustic signals are calibrated as a function of optical or physical head-disk spacing. When a wear test is carried out, time dependence of these signals with time provides a direct measure of the remaining film thickness or the local wear rate. The thin film wear rate is followed in situ with the above techniques and the final amount of wear is measured with ex-situ techniques. These new tribology techniques have been applied to comparison of the wear rates of thin ion beam and cathodic arc carbon films. The elastic modulus and nanohardness of these films were 150 and 230 GPa, and 23 and 55 GPa for ion beam and cathodic arc films, respectively. An adequate agreement was obtained between in situ and ex-situ measurements with film thickness resolution down to 1 nm and spatial resolution down to 200 nm. Cathodic arc carbon films showed significantly lower wear rates than ion beam deposited carbon films.

2:15 PM U10.3/V7.3

MICRO-WEAR SCAN TEST ON THE CARBON OVERCOATS AS THIN AS 6 NM OR LESS. T.W. Wu, IBM Almaden Research Center, San Jose, CA; T.W. Scharf, The University of Alabama, Center for Materials for Information Technology and the Department of Metallurgical and Materials Engineering, Tuscaloosa, AL; Hong Zhang, IBM Storage Systems Division, San Jose, CA.

The integrated mechanical strengths and failure mechanisms of ultrathin nitrogen-doped carbon overcoats (CNx) have been assessed by a micro-wear scan technique. These CNx coatings, with the thickness ranging from 1 to 6nm, were deposited on magnetic recording disks by a DC-sputtering process. In the course of a micro-wear scan, while the indenter is oscillating along the x-direction at a frequency of 2hz to perform the wear function, the tip scans at a speed of 0.18 um/sec along the y-direction with a gradual increased load. Because of this reciprocating, ramped-loading and scanning combined testing scheme, the micro-wear scan has a unique advantage to create a continuous wear track and preserve the wear morphology inside. Furthermore, a wear track of 20um by ~85um in size facilitates many surface analyses, such as high-resolution SEM and AES. A critical load, based on the first occurrence of coating damage, was used as a semi-quantitative measure of the mechanical strength of these overcoats. It was found that the critical load decreased in a nearly linear manner with the CNx thickness down to the ~2nm regime. However, the 1nm thick CNx coating deviated from this trend and its critical load decreased dramatically. High-resolution SEM was employed to reveal the details of the micro-wear pattern and the CNx failure mechanism will be illustrated and discussed.

2:30 PM U10.4/V7.4

ELASTIC CONSTANTS OF DIAMOND-LIKE CARBON FILMS BY SURFACE BRILLOUIN SCATTERING. A.C. Ferrari, J. Robertson, Engineering Dept, Cambridge University, UK; R. Pastorelli, M.G. Beghi, C.E. Bottani, Dip di Ingegneria Nucleare, Politecnico di Milan, ITALY.

The determination of the elastic constants of thin, attached films is extremely difficult. The reduced Youngs modulus is often extracted as from nano-indentation tests used to measure hardness. Laser-induced surface acoustic waves (SAWs) can also be used. The difficulties of using nano-indentation for hard thin films on softer substrates, such as tetrahedral amorphous carbon on Si, are well known. Whilst the hardness values derived by indentation for ta-C are found to be between 60 and 90 GPa. However, the Youngs modulus values derived by indentation are much more widely scattered, 400-1100 GPa. We show that Surface Brillouin Scattering (SBS), a SAW method, can for the first time determine all the isotropic elastic constants of hard-on-soft and soft-on-hard films, even less than 10 nm in thickness [1]. We find that the Youngs modulus, shear modulus and Poissons ratio of ta-C with a 88% sp³ fraction and 3.26 g/cm³ density are 757 GPa, 337 GPa and about 0.12 respectively. We find for ta-C:H with 70% sp³ and 30% hydrogen and 2.35 g/cm³ density these values are 300 GPa, 115 GPa and about 0.3. The data help to resolve the previous uncertainties in mechanical data. They show that the Youngs modulus of ta-C is less than diamond, while the moduli of ta-C:H are considerably less than those of ta-C because of the weakening effect of C-H bonding.

[1]A C Ferrari, et al, submitted to App Phys Lett.

2:45 PM U10.5/V7.5

TENSILE PROPERTIES OF AMORPHOUS DIAMOND FILMS. D.A. LaVan, J.P. Sullivan, T.A. Friedmann and C.I.H. Ashby, Sandia National Labs, Albuquerque, NM.

A computer-controlled Nanoindenter was used to test amorphous diamond samples in uniaxial tension by pulling laterally with a flat tipped diamond. Two sample designs were attempted. The first design was a single layer specimen where one end was rigidly attached to the substrate and the other had a ring that was engaged with the tip of the Nanoindenter. The second design was of two layers to permit the construction of samples with freely moving pivots at the fixed end. Tensile load is calculated by resolving the measured lateral and normal forces into the applied tensile force and frictional losses. Displacement is corrected for machine compliance using the differential stiffness method. Post-mortem examination of the samples was performed to document the failure mode. The load-displacement data from those samples that failed in the gage section was converted to stress-strain curves using the specimen cross section and gage length dimensions verified by measuring against a standard in the SEM. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

3:30 PM U10.6/V7.6

USING FINITE ELEMENT MODELING TO UNDERSTAND THE EFFECTS OF INDENTER SHARPNESS ON HARDNESS MEASUREMENTS OF THIN DLC FILMS ON Si SUBSTRATES. P.J. Wolff, E.G. Herbert, and B.N. Lucas, MTS Systems Corporation, Nano Instruments Innovation Center, Oak Ridge, TN.

The use of thin DLC films as mechanically protective overcoats is common in many aspects of the magnetic recording media industry. One technique that has been widely used to quantify the mechanical properties, specifically the hardness, of these films is depth-sensing indentation. However, it is well known that as the thickness of the film decreases, the ability to quantitatively determine properties from analytical techniques becomes increasingly difficult. This paper examines, from an experimental and FEM approach, the effect of indenter tip sharpness on the ability to accurately determine properties of 20 nm DLC films on Si substrates, a common industry configuration for testing. Experimental results for indenters with varying tip radii obtained using current analytical models will be compared to FEM calculations performed using indenters of the same, real geometry. The evolution of shear stress under the indenter will be presented in an effort to more clearly explain the measured results.

3:45 PM U10.7/V7.7

MICROCRYSTALLINE AND NANOCRYSTALLINE DIAMOND FILM DEPOSITION ON COBALT CHROME ALLOY. Marc D. Fries, Yogesh K. Vohra, Univ of Alabama-Birmingham, Birmingham, AL.

Medical implants ranging from tooth replacement posts to artificial hips, knees, and shoulders are commonly constructed of cobalt chrome alloy. These artificial human joints, in particular, are highly sensitive to wear and are usually replaced after ten years of use. In order to extend these implants' service lifetimes, a thin film of diamond will be applied to the implant wear surfaces by microwave plasma chemical vapor deposition (MPCVD) following MPCVD nitridation. Cobalt chrome often delaminates any deposited diamond film due to a high thermal expansion mismatch of 135 K^{-1} for cobalt chrome as opposed to only 1.13 K^{-1} for diamond. Additionally, cobalt chrome promotes the degradation of the growing diamond film into graphite, by absorption of carbon into the metal lattice. By nitriding the cobalt chrome through MPCVD prior to diamond deposition, a usable diamond film may be achieved. Since both nitridation and deposition will be performed by MPCVD, there is the possibility of merging the nitriding and deposition steps into a single process. We will also present experimental data on microcrystalline deposition as well as nitrogen-assisted nanocrystalline deposition. Residual stress will be analyzed through Raman laser spectroscopy and thin film X-ray diffraction (XRD).

Research supported by NASA EPSCoR and Alabama Space Grant Consortium

4:00 PM U10.8/V7.8

FABRICATION AND CHARACTERIZATION OF FUNCTIONALLY GRADIENT DIAMONDLIKE COATINGS. Q. Wei¹, A.K. Sharma², S. Yarmolenko¹, J. Sankar¹ and J. Narayan², NSF Center for Advanced Materials and Smart Structures. ¹ Dept of Mechanical Engineering, McNair Hall, North Carolina A&T State University, Greensboro, NC, ²Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

Pure diamondlike carbon thin films largely bonded by four-fold

coordination suffer from a large internal compressive stress that gives rise to serious adhesion problem. In this work, functionally gradient diamondlike carbon thin coatings were prepared by pulsed laser deposition in a high vacuum as an alternative approach to address the adhesion problem of diamondlike films. Copper, silver and titanium were incorporated into the growing films with their concentration as a function of distance from the substrate surface. The top of the thin coatings is pure DLC of about 400 nm in thickness. Nanoscale mechanical characterizations using Nanoindenter XP[®] were carried out to study the mechanical behavior of the functionally gradient DLC films. Scratch tests were made to assess the improvement in adhesion.

4:15 PM U10.9/V7.9

NANOMECHANICAL PROPERTIES OF AMORPHOUS CARBON AND CARBON NITRIDE THIN FILMS PREPARED BY SHIELDED ARC ION PLATING. Nobuhiro Tajima, Hiroki Saze, Hiroyuki Sugimura and Osamu Takai, Department of Materials Processing Engineering, Graduate School of Engineering, Nagoya University, Nagoya, JAPAN.

Hydrogen free amorphous carbon (a-C) and carbon nitride (a-C:N) were synthesized by means of shielded arc ion plating in which a shielding plate was inserted between a target and a substrate in order to reduce macroparticle deposition onto the substrate [1]. Thin films of a-C and a-C:N were prepared in an arc discharge plasma of argon or nitrogen gas, respectively, at a pressure of 1 Pa by using a graphite target as cathode. Mechanical properties of these films was studied in relation to substrate bias voltage with a nanoindenter. The a-C film prepared at a bias of -100 V consisted of diamond-like phase and showed a maximum hardness of 35 GPa, whereas the film deposited at a bias of -500 V had a minimum hardness of 7 GPa indicating that the film was converted to be graphite-like due to excessive ion impact in the Ar plasma. The wear resistance of the a-C films depended on the hardness, namely, harder a-C films were more wear resistant. On the contrary, the hardness of the a-C:N films, which remained in the range of 10 to 14 GPa, was less dependent on the bias voltage and much lower than the maximum hardness of the a-C films. Nevertheless, the wear resistance of the a-C:N films was comparable to or better than the a-C films. In particular, the a-C:N film prepared at a bias of -300 V was so wear resistant that the film did not wear at all when rubbed with a diamond tip at a contact force of 20 μN . The presence of $\beta\text{-C}_3\text{N}_4$ like phase characterized by a N1s XPS peak at 400.5 eV has found to be crucial for wear resistance of the a-C:N films. [1] Y. Taki, T. Kitagawa and O. Takai, This Solid Films, 304 (1997) 183.

4:30 PM U10.10/V7.10

INTRINSIC STRESS MEASUREMENTS IN CVD DIAMOND FILMS. J.G. Kim, Hyundai Electronics Ltd., Ichon, KOREA; Jin Yu and Y.C. Sohn, KAIST, Dept of Materials Science and Engineering, Taejeon, KOREA.

Diamond films were grown over the (100) Si substrate by the hot filament CVD method using the CH_4/H_2 gas mixture with varying CH_4 content, and the substrate curvatures were measured ex-situ at various stages of the film growth. In order to measure the intrinsic stress in the film, substrate curvatures originating from the substrate creep and the thermal stress associated with the ex-situ measurements were carefully taken into account. Creep deformation of the Si substrate due to the thin film stress at the CVD temperature was measured after removing the diamond layer using the reactive ion etching method. Results showed that the intrinsic stress in the film as always positive increasing with the film thickness and decreasing with the CH_4 content, and that a failure to consider creep of the substrate would overestimate the film stress by more than a factor of two. Later an elastic/plastic analysis was conducted to calculate the creep strain and deduce the intrinsic stress without tedious diamond etching process. The method involved analysis of the bend creep and showed reasonable agreement with the experiment. Finally, in order to understand the origin of the intrinsic stress in the diamond film, an analysis based on the density and grain size measurements of diamond films showed that intrinsic stress evolved mainly out of the grain growth during the film thickening.

4:45 PM U10.11/V7.11

REDUCING INTRINSIC STRESS BY CONTROLLING GRAIN BOUNDARY FORMATION. Brian W. Sheldon, Ashok Rajamani, Janet Rankin, Rod Beresford, Brown University, Division of Engineering, Providence, RI; Barbara L. Walden, Trinity College, Physics Department, Hartford, CT.

The primary objective of this research is a better understanding of the relationships between intrinsic stress and grain boundary formation. This work involved experiments with several different materials, including CVD diamond and epitaxial nitrides. In all of these cases, significant tensile stress evolves during island coalescence, and large reductions in this intrinsic stress were obtained by controlling the coalescence process. In particular, changes in the deposition chemistry

during coalescence can have a significant effect on the resultant intrinsic stress. Stress was monitored by using bending plate curvature measurements, and films were also characterized with electron microscopy, Raman spectroscopy, and x-ray diffraction. In addition to the experimental results, mathematical models have been created to describe how the film structure evolves. These efforts demonstrate that stress evolution during island coalescence can be strongly affected by different kinetic mechanisms and by island morphology.

SESSION U11: STRUCTURAL CHARACTERIZATION OF AMORPHOUS CARBON

Chairs: Michael P. Siegal and John P. Sullivan
Thursday Morning, December 2, 1999
Room 311 (H)

8:30 AM *U11.1 MEDIUM-RANGE ORDER IN AMORPHOUS CARBON STUDIED BY FLUCTUATION ELECTRON MICROSCOPY. J. Murray Gibson, Argonne National Laboratory, Argonne, IL.

We have developed a new quantitative transmission electron microscope method fluctuation microscopy[1] which probes medium-range order in amorphous thin films. From statistical measurements of speckle in dark-field images we can determine the nature of higher-order atomic correlation functions. Whereas the diffraction pattern alone can give only the pair correlation function, which is very sensitive to medium-range order, fluctuation microscopy reveals the 4-body pair-pair correlation function, which is sensitive to medium-range order. Our first experiments had examined tetrahedral amorphous semiconductors. For these we have found that as-grown structures typically show much more order than the continuous random network, and we have described them by paracrystalline models[2-4]. However, thermal annealing causes a reduction in medium-range order and a transition towards the continuous random network state. In this paper, I will describe more recent results on amorphous carbon. We are studying a number of types of amorphous carbon, including hydrogenated samples, and will discuss the extent of medium-range order, and its possible relationship to physical properties. In particular we will compare diamond-like amorphous carbon to amorphous silicon and germanium. 1. Treacy, M.M.J. and J.M. Gibson, *Acta Crystallogr.*, 1996. A52: p. 212. 2. Gibson, J.M. and M.M.J. Treacy, *Phys. Rev. Letts.*, 1997. 78: p. 1074. 3. Treacy, M.M.J. and J.M. Gibson, *J. Non-Cryst. Solids*, 1998. 231: p. 99. 4. Gibson, J.M., et al., *Appl. Phys. Letts.*, 1998. 73: p. 3093.

9:00 AM *U11.2 CHARACTERIZATION OF NANOSTRUCTURED CARBON FILMS. M.P. Siegal, D.L. Overmyer, D.R. Tallant, J.C. Barbour and P.N. Provencio, Sandia National Laboratories, Albuquerque, NM.

Diamondlike amorphous carbon (a-C), nanocrystalline graphite, nanocoralline, fullerenes and nanotubes are all nanostructural forms of pure carbon. Only a-C films consist of a mixture of both 3- and 4-fold coordinated carbon atom nanoclusters. The ratio of bond types can be controlled via the energetics of growth, resulting in films that are ultrahard, optically transparent and electrically insulating to films that are soft, opaque and conductive. The other pure carbon materials consist of graphene sheet structures with very different nanostructural/morphological features. Not surprisingly, the electrical, optical and mechanical properties of these materials are dominated by their structures. Comparisons will be made between a-C, nanocoralline and aligned nanotube films. Potential applications for each of these interesting forms of carbon films will be discussed.

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

9:30 AM U11.3 RAMAN SIGNATURES OF BONDING AND DISORDER IN CARBONS. A.C. Ferrari, J. Robertson, Engineering Dept, Cambridge University, UK.

Raman spectroscopy is the most popular non-destructive technique to monitor the bonding in diamond-like carbons (DLC) and the degree of disorder in micro-crystalline graphites. However, such analysis is risky, first because of the low cross-section of sp³ sites and second because the intensity ratio of the D and G peaks must ultimately reduce for small sp² grains, and not increase continuously for small crystallites as implied by the Tuinstra-Koenig relationship. We have been able for the first time to separate how four factors control the G and D peaks in the visible Raman spectrum of disordered carbons - the sp² clustering or grain size, the loss of graphitic ring structure, the relative fraction of graphitic rings and olefinic chains, and the sp³ fraction. In general the visible Raman spectrum depends on the 'quality' of the sp² bonding and only indirectly on the sp³ fraction. A

key observation is that the clustering of sp² sites can be varied at constant sp³ content in high sp³ solids by post-deposition annealing of tetrahedral amorphous carbon (ta-C), and in high sp² material by ion bombarding glassy carbon. In amorphous carbon, the G peak moves up due to three factors; higher sp² content, perfection of the graphitic rings, and replacing sp² graphitic rings by olefinic chains. These rules allow us to state when we can relate the shift in G peak simply to the sp³ content of DLCs.

9:45 AM U11.4 IN-SITU SCANNING TUNNELING MICROSCOPIC AND SPECTROSCOPIC INVESTIGATION OF MAGNETRON SPUTTERED CARBON AND CARBON NITRIDE THIN FILMS. Nian Lin, Niklas Hellgren, Mats P. Johansson, Lars Hultman, Ragnar Erlandsson, Department of Physics, Linköping University, Linköping, SWEDEN; Jan-Eric Sundgren, Chalmers University of Technology, Göteborg, SWEDEN.

Carbon and carbon nitride films, grown in argon or nitrogen discharges by reactive d.c. magnetron sputtering of a graphite target, were characterized by in-situ scanning tunneling microscopy. When the growth temperature increased from ambient to 800°C, we observed a topographic evolution of the carbon films from an amorphous to a graphite-like structure, and further to a distorted-graphitic phase with curved and intersecting basal planes, and finally to a surface containing nanotubes and nanodomains. When nitrogen was incorporated into the films, distortion of the graphitic basal planes occurred at a lower temperature compared to the pure carbon case. At temperatures of ~200°C and above, regions of a non-graphitic phase, containing a high degree of carbon sp³-bonds were observed. Spatially resolved tunneling spectroscopic measurements indicated that the band gaps were 0, ~0-0.6 eV, and ~0.4-2.0 eV for graphite-like structures, the distorted-graphitic phase, and the non-graphitic phase, respectively. Together with ex-situ x-ray photoelectron spectroscopy and reflection electron energy loss spectroscopy measurements, the results suggest that the incorporation of nitrogen promotes bending of the graphitic basal planes and thereby facilitates the formation of three-dimensional covalently bonded networks with a high degree of sp³-coordinated carbon atoms.

10:30 AM U11.5 RANGES AND MIXING OF CARBON IONS DURING GROWTH OF TETRAHEDRAL AMORPHOUS CARBON FILMS. H. Hofsäss, H. Feldermann, C. Ronning, Universität Göttingen; Physikalisches Institut, GERMANY; G. Dollinger, A. Bergmaier, S. Karsch, O. Schmelmer, Physik-Department, Technische Universität München, GERMANY.

The deposition of energetic carbon ions is a suitable method to produce diamondlike amorphous carbon films with a large fraction of sp³-coordinated carbon atoms. The number of sp³ bonded carbon atoms depends on the kinetic energy of the impinging ions and correlates with many physical properties of the films like the density, the hardness, the electric conductivity and the bandgap. A maximum of the sp³ bonded fraction around 80% is obtained for ion energies between about 100 eV to 300 eV. Obviously the change of the properties of the carbon films is correlated to the penetration behaviour, the energy release and the ranges of the carbon ion. Up to now these parameters are determined from extrapolations of binary atom-atom potentials, which may not hold at such low ion energies. Therefore, experimental data are needed in order to give relevant input data to growth models. ¹²C/¹³C multilayer films were prepared by depositing energy selected carbon ions (50 eV to 1 keV) on silicon substrates in UHV. About 20 nm thick layers were prepared using a ¹²C beam. δ -layers consisting of 5×10^{14} at/cm² ¹³C were deposited at a depth of about 5 nm below the surface and at the very surface using different ion energies. The ranges and the mixing of the deposited ¹³C ions were quantitatively measured using high resolution elastic recoil detection analysis. The data show an increasing range of the ¹³C ions which is 0.5 nm for 100 eV ions and 1.2 nm for 500 eV. The measured ranges are significantly lower than calculated with TRIM. The width of the buried δ -layer is larger than the range of the ions showing clearly the effect of mixing processes occurring during film growth.

10:45 AM U11.6 STRUCTURE AND BONDING IN MASS-SELECTED ION-BEAM DEPOSITED CARBON FILMS. J. Kulik, University of Houston, Texas Center for Superconductivity, Houston, TX; G. Lempert, E. Grossman, and Y. Lifshitz, Soreq NRC, Yavne, ISRAEL.

Mass-selected ion-beam deposition has been used to grow carbon films on Si substrates. The structure and bonding of the resulting non-crystalline films have been characterized by transmission electron microscopy and electron energy loss spectroscopy. Depositions were done with an energy of 120 eV at a substrate temperature of 200 C and also with higher energies (10 to 20 keV) at ambient temperature.

For the 120 eV deposition at 200 C the resulting film is sp² bonded and oriented such that the graphitic sheets stand normal to the substrate (pi-bonds parallel to the substrate). Moreover, the film is under significant bi-axial stress such that the graphitic layer spacing is reduced by 4% from that of ambient pressure graphite. At high energies (> 10 keV) there is also a similar preferred texture to the film, but with very likely a different origin, i.e., the texturing in this case is likely caused by atomic displacements due to the impinging ion beam together with the anisotropic displacement threshold for sp² bonded carbon. At 20 keV, the film evolves into a novel bi-layered structure with the lower layer having graphitic sheets normal to the substrate and an upper layer with the sheets preferentially oriented parallel to the substrate.

11:00 AM U11.7

THE EFFECT OF ADDING NITROGEN TO AMORPHOUS HYDROGENATED CARBON: A STUDY USING NEUTRON, FTIR AND NMR SPECTROSCOPES. Mark A. Holland, Dave M. Pickup, Bob Newport, Univ. of Kent at Canterbury, School of Physical Sciences, Canterbury, UK; Jennifer K. Walters, University College London, Dept. of Physics and Astronomy, London, UK; Iain J.F. Poplett, Univ. of Warwick, Dept. of Physics, Coventry, UK.

We report the hitherto unpublished results of a study of the structural properties of a series of nitrogen doped amorphous hydrogenated carbon, a-C:N:H, samples using incoherent inelastic neutron scattering, neutron diffraction, Fourier transform infra red spectroscopy and ¹H, ¹³C and ¹⁵N solid state NMR. The samples were made using a fast-atom beam deposition system in which the ionised precursor fragments are neutralised as they exit the saddle field ion source. Precursor gases used were acetylene, C₂H₂, ammonia, NH₃ and nitrogen. Nitrogen contents as high as 10 at.% were achieved, with hydrogen contents falling in the range 16 - 25 at.%. The data, which complements earlier diffraction work [J Phys: Condens Matt., **8**, 4739, 1996; J. Appl. Phys. **83**, 3529, 1998], reveals the presence of a range of bonding types, including C≡N. The results are interpreted in the light of existing knowledge regarding the a-C:H host network structure [J. Phys: Condens Matter **7**, 1755, 1995] and linked to the observed macroscopic optical, electrical and mechanical properties of a-C:N:H materials. It is observed that H bonds to N in preference to either sp² or sp³ carbon sites, but that neither the overall concentration of CH₂ (olefinic and aromatic) groups nor the sp²:sp³ carbon ratio alters significantly with N content. There is, however, some variation of imide (-C=N) and amide/ammonium (-NH/NH₂) content. The structure remains amorphous at all nitrogen concentrations, and there is no evidence of graphitic ring formation.

11:15 AM U11.8

STRUCTURAL AND ELECTRONIC PROPERTIES OF FLUORINE IMPURITIES IN TETRAHEDRALLY BONDED AMORPHOUS CARBON. G. Jungnickel, Th. Frauenheim, G. Seifert, Universitaet Gesamthochschule Paderborn, Paderborn, GERMANY.

We have applied the density-functional based tight-binding (DFTB) method to study the incorporation of fluorine in tetrahedral amorphous carbon (ta-C). Experimental findings in graphite intercalation compounds where F atoms seem to stimulate the formation of 4-fold coordinated carbon caused us to carefully check the ability of F dopants to improve the structural and electronic properties of the amorphous carbon material with respect to electronic applications. We observe a competition of local structures where Fluorine is truly covalently bonded to the carbon network and configurations where Fluorine traps an electron, becomes inert, and exists unbonded in microvoids. We discuss the charge transfer effects between Carbon and Fluorine and evaluate their importance by the recently developed self-consistent charge tight-binding technique.

11:30 AM U11.9

CHARACTERIZATION AND DIELECTRIC PROPERTIES OF FLUORINATED AMORPHOUS CARBON MEASURED BY CAPACITANCE-VOLTAGE VERSUS SPECTRAL ELLIPSOMETRY. Alexander D. Glew, Stanford University, Dept. of Material Science and Engineering; Mark A. Cappelli, Stanford University, Dept. of Mechanical Engineering, Stanford, CA.

In this work, we have deposited fluorinated amorphous carbon (FLAC) films on Si substrates. FLAC is a low k dielectric material. The impinging ion energy is systematically varied in order to study the effects on the film properties. The film density and mass deposition rate are evaluated by gravimetric methods. The film stress is measured by recording the change in curvature with laser reflection. The F:C ratio of the film is determined by x-ray photoelectron spectroscopy (XPS). Also, we have fabricated metal-oxide-silicon (MOS) devices in order to measure the dielectric properties of the film by a standard capacitance-voltage (C-V) method. The C-V measurement results for dielectric constant are compared to previous measurements by spectral ellipsometry. It is desirable to know the

relationship between the C-V method, which requires special structures and is destructive, and the non-destructive spectral ellipsometry.

11:45 AM U11.10

FLUORINE INCORPORATION INTO HARD AMORPHOUS HYDROGENATED CARBON FILMS DEPOSITED BY PECVD. F.L. Freire, Jr., L.G. Jacobsohn, Pontificia Universidade Catolica do Rio de Janeiro, Departamento de Fisica, Rio de Janeiro, BRAZIL; D.F. Franceschini, Instituto de Fisica-UFF, Niteroi, BRAZIL.

We investigate the incorporation of fluorine into amorphous hydrogenated carbon films (a-C:F:H) deposited by the plasma enhanced chemical vapor deposition technique (PECVD). Different mixtures of CH₄ and CF₄ were employed as the plasma pressures. While the total pressure was fixed at 10 Pa in all depositions, the inlet flux of each gas could be varied such that the total inlet gas flux was 3 sccm. Films of a-CH:F were deposited with the partial pressure of CF₄ ranging from 0 to 85%. The self-bias was kept at -350 V. The composition of the films was determined by Rutherford backscattering spectrometry (RBS) and by elastic recoil detection analysis (ERDA). These results, together with the film thickness as measured by stylus profilometry, provided the atomic density. While the hydrogen content was nearly constant and around 20 at.%, a fluorine incorporation of 30 at.% was achieved for partial pressures of CF₄ of 85%. It was also found that the incorporation of fluorine has the effect of reducing the internal compressive stress. While a-C:H films have an internal compressive stress of around 3 GPa, for films deposited in atmospheres with partial pressure of CF₄ of 85% the internal stress decreases down to 1 GPa. Finally, the growth mechanism of a-C:H:F films was investigated: the increase of the CF₄ partial pressure from 0 to 85%, results in an increase of the deposition rate from 13 to 21 nm/minute. In the case of a pure CF₄ atmosphere, for the plasma conditions described above, only substrate erosion, instead of film deposition, was observed.

SESSION U12: DEPOSITION AND ELECTRICAL PROPERTIES OF AMORPHOUS CARBON

Chairs: Tatiana Allen and Stefan Zukotynski
Thursday Afternoon, December 2, 1999
Room 311 (H)

1:30 PM *U12.1

HYDROGENATED AMORPHOUS CARBON DEPOSITED BY SADDLE-FIELD GLOW DISCHARGE. Stefan Zukotynski, University of Toronto, Dept of Electrical and Computer Engineering, Toronto, Ontario, CANADA.

The presence of two distinct atomic hybridizations, sp³ and the sp², is the main factor responsible for the very wide range of properties of hydrogenated amorphous carbon (a-C:H). The dc saddle-field glow discharge is characterized by unusually large fluxes of high energy electrons at the anode and the deposition system based on this principle has been shown to produce a-C:H films with sp³ content varying from 30% to 85%. The large changes in structure are reflected in the optical and electrical properties of a-C:H. Results of Monte Carlo simulation of the saddle-field discharge will be presented, the main characteristics of the deposition system will be described and its plasma properties will be compared with standard deposition techniques. The effect of these properties on the characteristics of a-C:H will then be presented. In particular, we will examine optical characteristics, such as luminescence, and electrical conductivity. We will argue that a-C:H can behave as a true semiconductor that can be effectively doped both n- and p-type.

2:00 PM *U12.2

FREE AND BONDED HYDROGEN IN a-C:H. Vladimir Ivanov-Omskii, A.F. Ioffe Physical-Technical Institute, St. Petersburg, RUSSIA.

Although various properties of amorphous hydrogenated diamond-like carbon (DLC) are known to be controlled by hydrogen incorporated into the disordered carbon network, the information on real hydrogen states in DLC is available mostly for those covalently bonded with carbon atoms. Recent results obtained by our group on IR absorption and vacuum UV Raman spectroscopy show that, along with the hydrogen state covalently bonded with carbon, there exists a quasi-free state of stretched H₂ molecules adsorbed by graphite-like structural fragments. Vanishing of the bonded states of hydrogen at temperatures above ~500°C was reported by many authors. However, our group succeeded to show that degradation of the bonded states at temperatures below ~450°C may be reversible, at least partially. A model of thermally induced reversible transfer of hydrogen between the bonded and non-bonded states is suggested to describe the experimental results on the IR spectroscopy of thermally treated DLC.

2:30 PM U12.3

FILTERED CATHODIC ARC DEPOSITED DIAMOND LIKE CARBON: ELECTRON SPIN RESONANCE (ESR) AND RAMAN SPECTROSCOPY. Boris Druz, Isaak Zaaritskiy, Yuriy Yevtukhov, Veeco Instruments, Inc., Plainview, NY; Andrey Konchits, Mikhail Valakh, Sergey Kolesnik, Bela Shanina, Victor Visotski, Institute of Semiconductor Physics, Kiev, UKRAINE.

Diamond like carbon (DLC) films were deposited onto high resistive Si substrates using Filtered Cathodic Arc (CADLC) process. Hardness of the deposited films was 45÷55 GPa, Young Modulus - 240 - 280 GPa, while stress was varied significantly (2.5÷8.5 GPa). The stationary and pulse ESR techniques were used to analyze defects in the pseudo-gap of undoped, as deposited 20 - 100 nm thick films. The measurements were performed in temperature range T=1.75-300K to characterize paramagnetic center parameters: spin density N, line-width ΔH_{pp} , resonance magnetic fields (g-values), microwave saturation, spin-spin and spin-lattice relaxation rates. High density of the centers $N=(1.8\div 3.1)10^{21} \text{ cm}^{-3}$ was observed in the films. N and ΔH_{pp} were correlated with the films internal stress: the more stress, the more N and ΔH_{pp} . According to microwave saturation data the centers were distributed in clusters. ESR signal anisotropy (anisotropy of g- and ΔH_{pp} parameters), giving an evidence of structural anisotropy, was found at low temperature for the first time. The observed phenomena can be related to induced by spin-spin interaction macroscopic magnetization in the films which is becoming significant at high density of the centers. Magnetic anisotropy is, probably, related to preferential orientation of sp^2 bonds in the films with respect to the substrate surface. The Raman spectra of CADLC exhibited the typical for these materials unresolved peak at 1540-1570 cm^{-1} . Raman shift of this peak allowed us to estimate $sp^2/(sp^2+sp^3)$ ratio ~ 0.15 and 0.35 for high and low stress films respectively. The results are compared with data for direct ion beam deposited from CH_4 plasma hydrogenated DLC films and nature of paramagnetic defects in DLC is discussed.

2:45 PM U12.4

PLASMA DIAGNOSTICS DURING PULSED LASER DEPOSITION OF DIAMOND-LIKE CARBON USING SINGLE CRYSTAL GRAPHITE AND AMORPHOUS CARBON. Yukihiko Yamagata, Ajay Sharma, Jagdish Narayan, NSF Center for Advanced Materials and Smart Structures, North Carolina State Univ., Dept of Materials Science and Engineering, Raleigh, NC; Robert M. Mayo, James W. Newman, North Carolina State Univ., Dept of Nuclear Engineering, Raleigh, NC; Kenji Ebihara, Kumamoto Univ., Dept. of Electrical and Computer Engineering, Kumamoto, JAPAN.

Pulsed laser deposition (PLD) has been employed to fabricate superior quality diamond-like carbon (DLC) films with sp^3 formation exceeding 80%, high fullerene carbon molecules and carbon nanotube. The mechanism of the PLD process, however, has not yet been well understood. Optical emission spectroscopy (OES) is one of powerful tool to diagnose the laser ablation plasma plume, and is useful to establish correlation between plasma composition and properties of deposited films. In this paper, we describe systematic studies using OES¹ and Langmuir probe² on the plasma plumes generated by KrF excimer laser irradiation on a single crystal graphite and an amorphous carbon in vacuum and nitrogen atmosphere. In high vacuum, the emission lines from carbon ions of C^+ , C^{2+} and C^{3+} have been observed in addition to several atomic carbon lines in both targets. In a nitrogen atmosphere, band emissions of CN and C_2 molecules are detected and those intensities increase with pressure. As for the amorphous carbon target, the vibrational temperature of CN is very high for 2 μs after the laser pulse and is consistent with the kinetic energy of C^+ , while that for subsequent 50 μs is as low as 1.3 eV and decreases slightly with pressure increase. The vibrational temperature of C_2 is almost constant at 0.6 eV, which is consistent with the electron temperature. It is conjectured that CN molecules are formed directly in reactions involving energetic ionic monatomic carbon, and that the formation of excited C_2 molecules are the result of molecular recombinations of C atoms and ions. The nanohardness of deposited films decreases with increase of the emission intensity ratio of C_2/C . From the OES results and the characteristics of deposited films, it is suggested that the C_2 molecule in the ablated plasma plume is not conducive, but energetic species, such as C^+ , are very important for producing of high quality DLC films using PLD.
¹Y. Yamagata, A. Sharma, J. Narayan, R.M. Mayo, J.W. Newman, K. Ebihara, J. Appl. Phys. in press, (1999).
²R.M. Mayo, J.W. Newman, A. Sharma, Y. Yamagata, J. Narayan, J. Appl. Phys. in press, (1999).

3:30 PM U12.5

PARTIAL CARBONIZATION OF AROMATIC POLYIMIDE FILMS. Masao Doyama, A. Ichida, Y. Inoue, Y. Kogure, T. Nozaki and S. Yamada, Teikyo University of Science & Technology, Uenohara, Yamanashi, JAPAN.

Aromatic polyimide films, Upilex S are partially carbonized between 700°C and 1000°C. Electrical conductivity and Hall effect coefficient have been measured. Electrical conductivity is higher at higher temperatures. The electrical conductivity s could be expressed as $s = s_0 \exp(-E/kT)$ eq(1), where k is the Boltzman constant. T is the absolute temperature. s_0 and E are found to be $4 \times 10^{-5} \text{ W}^{-1} \text{ m}^{-1}$ and 0.02eV, respectively. The electrical conductivity of the film carbonized in hydrogen atmosphere was higher than that carbonized in nitrogen atmosphere. It is likely that hydrogen was caught by dangling bonds so that the mean free path of carriers is longer in the film carbonized in hydrogen atmosphere than those carbonized in nitrogen atmosphere. The experimental data show the Hall coefficient R is negative, and this implies the carriers are negatively charged, i.e. electrons. The specimens are n-type semiconductors. The carrier density n_e is given by $n_e = (|e|R)^{-1}$ and the mobility $\mu_e = s / (n_e |e|)$, where $|e|$ is the absolute value of the electron charge and s is the electrical conductivity. Fitting $n_e = A_1 \exp(-E_1/kT)$ and $\mu_e = A_2 \exp(E_2/kT)$. One finds $A_1 = 30.13 \text{ m}^{-3}$, $E_1 = 0.067 \text{ eV}$ and $A_2 = 1.643 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $E_2 = 0.047 \text{ eV}$. The electrical resistivity ρ is given by $\rho = 1/s = 1/n_e \mu_e = 1/A_1 A_2 \exp[(E_1 + E_2)/kT]$. $E_1 + E_2 = -0.067 + 0.047 \text{ eV} = 0.02 \text{ eV}$. This is consistent with eq. (1). The polyimide films are not completely carbonized but partially carbonized at 1000°C. The partially carbonized polyimide is an n type donor. It is concluded that the impurity level lies about 0.02eV below the conduction band. This research is partially supported by Ube Industries, Ltd. We are particularly thankful to Drs. R. Sato and S. Hashiguchi at Ube Industries, Ltd.

3:45 PM U12.6

AB-INITIO STUDY OF BORON DOPING IN TETRAHEDRAL AMORPHOUS CARBON. Alfredo Gambirasio, Marco Bernasconi, INFN and Milano-Bicocca Univ, Dept of Materials Science, Milano, ITALY.

Thin films of tetrahedral amorphous carbon (ta-C) are grown via implantation of energetic carbon ions on a substrate. The local compressive stress generated in the implantation process is believed to be the most important factor favoring the formation of a high fraction of four-fold coordinated carbon atom (> 60%). However, the large stress limits the film thickness to few tens of nanometer and represents the main hindrance to technological applications of ta-C. It has been shown experimentally that a possible way to overcome this difficulty is the doping of ta-C with small concentration (2-4%) of boron in the growth process. In fact boron can reduce the internal stress without changing appreciably the fraction of sp^3 atoms [Chhowalla *et al*, Appl. Phys. Lett. **69**, 2344 (1996).] We here present an ab-initio study of the effects of boron incorporation in ta-C using Car-Parrinello first-principle molecular dynamics. Samples at density of 2.9 g/cm^3 with boron concentration of 1.6% and 3.2% are generated by quenching from the liquid phase. In agreement with EELS measurements we find that boron occupies mostly sp^2 sites and does not affect the fraction of sp^3 carbon atoms. Moreover boron preferentially substitutes carbon in highly stressed 3-membered rings. The boron incorporation induces the opening of the ring which might be the mechanism leading to stress release by boron. The analysis of the electronic properties reveals that the presence of boron does not induce, in any case, shallow acceptor levels in the gap.

4:00 PM U12.7

ELECTRONIC PROPERTIES OF DIAMOND/AMORPHOUS CARBON HETEROSTRUCTURES. P. Reinke, P. Oelhafen, Universität Basel, Institut für Physik, Basel, SWITZERLAND.

The formation and electronic properties of heterostructures consisting of diamond and amorphous carbon layers, which are often also formed unintentionally during the processing of diamond surfaces, are of considerable interest in order to tailor and understand the properties of pure carbon structures. Structurally different amorphous carbon films, namely sp^2 amorphous carbon (a-C), and a-C:H (200 and 600 eV ion energy) films, with a thickness of 0.1 to 100 monolayers (ML) are deposited onto boron-doped polycrystalline diamond films. Photoelectron spectroscopy in the ultraviolet (UPS) and X-ray regime (XPS) is performed in-situ and yields information on the electronic structure of both participating layers and the interface. The structure of the amorphous overlayers is not influenced by the interaction with the crystalline diamond and no interfacial region which deviates structurally from the substrate or the overlayer is observed. In diamond/a-C a downward band bending in diamond evolves continuously with overlayer thickness and a final value of about 1.1 eV is obtained, resulting in a band offset of $1.5 \pm 0.1 \text{ eV}$. In the diamond/a-C:H structure a downward band bending of 1.4 eV and band offset of $1.4 \pm 0.15 \text{ eV}$ is observed and the role of defects in the pinning of the fermi level at the surface is ascertained by a comparison with ion irradiated diamond surfaces. It is evident that the presence of surface defects and other sp^2 bonded structures with states located energetically in the gap of diamond, changes the

electronic properties of the surface decisively and can therefore alter the electron emission properties. This knowledge can also be exploited to create structures with well defined band bending/valence band offset by depositing overlayers with variable band gaps, but excluding defect-creating energetic ions during the deposition.

4:15 PM U12.8

ELECTRICALLY CONDUCTIVE DIAMOND-LIKE CARBON FILMS BY RF PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION. Woon Choi, Yangdo Kim, Fukuoka Industry, Science & Technology Foundation (Fukuoka, IST), Fukuoka, JAPAN; Akira Adachi, Hajime Tomokage, Fukuoka Univ, Dept of Electronics Engineering and Computer Science, Fukuoka, JAPAN; Yoichi Iseri, Kyushu Mitsumi Ltd, Fukuoka, JAPAN; Toshihiro Ando, Core Research for Evolutional Science Technology (CREST), Ibaraki, JAPAN; Donghwan Kim, Div of Materials Science & Engineering, Korea Univ, KOREA.

Nitrogen-doped diamond-like carbon (DLC) films were deposited on both p+ and n+ silicon substrates by rf plasma enhanced chemical vapor deposition (PECVD) method using a mixture of CH₄ and N₂ gaseous source. RF power with negative dc bias voltage was applied to water-cooled substrate holder. The upper anode electrode grounded electrically was specially designed to enhance the thermal decomposition of reactant gases. Total reactant gas pressures were fixed on 10mTorr and nitrogen partial pressures were varied from 0.1 to 0.4. Working pressure was measured using capacitance manometer and the base pressure was kept constant to be 4X10⁻⁶ Torr using turbo molecular pump. The Raman spectra measured in all samples deposited showed clear separation of D (nearly 1380cm⁻¹) and G (nearly 1575cm⁻¹) bands. Electrical resistivity was measured by four-point probe method as a function of self-bias voltage V_s. Resistivity decreased with decreasing V_s and a minimum resistivity of 0.1 ohm-cm was obtained at V_s=-1300V. The film had a very smooth surface and the surface roughness was ascertained to be about 3nm by scanning tunneling microscope. In order to perform electrical measurements, aluminum and gold electrodes were formed by vacuum evaporation. Current-voltage characteristics between the electrode and silicon substrate (p+ and n+, respectively) showed the Schottky barrier characteristics at the interface between metal and n-type DLC. Electron beam-induced current (EBIC) technique was applied to the sample on n-type silicon substrate. The EBIC contrast under the aluminum contact was observed, which indicates that the depletion region was formed due to the Schottky barrier.

4:30 PM U12.9

PHOTOCONDUCTIVITY AND PHOTOLUMINESCENCE OF AMORPHOUS CARBON NITRIDE a-CN_x FILMS PREPARED BY THE LAYER-BY-LAYER METHOD. T. Katsuno^a, S. Nitta^a, H. Habuchi^b, T. Iwasaki^a, T. Itoh^a, and S. Nonomura^a, ^aDept of Electrical Engineering, Gifu University, Gifu, JAPAN; ^bDept of Electrical Engineering, Gifu National College of Technology, Shinsei-chou, Motosu, Gifu, JAPAN.

A-CN_x films prepared in our laboratory show high photosensitivity S_p with the photo-conductivity- and dark- conductivity ratio σ_p/σ_d of 10³ ~ 5x10⁶ which is interesting to applications as photoconductors {1}~{3}. All a-CN_x films used in this experiment are made by the layer-by-layer method with the deposition of CN_x and the etching by atomic hydrogen alternately controlled by a microcomputer. Typical conditions of sputtering of carbon target are rf-power of 85W, N₂ sputtering gas of 0.12Torr and the substrate temperature T_s of 200°C. For the etching of a-CN_x, hydrogen radicals are prepared with H₂ of 0.5 Torr at the same temperature and rf-power as the deposition. Typical one process to prepare LLa-CN_x film consist of (a) a deposition of a-CN_x layer about 35 nm by nitrogen plasma sputtering a carbon target for 600 s, (b) evacuating for 30 s, (c) an etching about 20 nm with hydrogen plasma for 100 s and (d) evacuating for 30 s. Resulting, photoconductive sensitivity of LLa-CN_x films is about 5x10⁶ which is 50times larger than that of a-Si:H. Spectral dependence of photoconductivity for LLa-CN_x films is studied. At a constant photon number, the photocurrent of LLa-CN_x films increase gradually from 1.5 to 4 eV. This increase can be explained by the increase of absorption coefficients with photon energy. The saturation of photocurrent is not observed until 4 eV. Therefore we are preparing to extend the spectral dependence of photoconductivity to higher energy range. Photocurrents I_p of LLa-CN_x films depend on the excitation photon energy I. For examples, I_p of LLa-CN_x films at 3 and 4 eV increase following I^{0.86} and I^{1.13} respectively. The degradation of photocurrent is observed at the excitation of 4.1 eV which is explained tentatively as a degradation by the increase of surface defect density. Photoluminescence spectra of LLa-CN_x films show broad peaks at 1.4 eV and at 1.85 eV. These results will be discussed with data of ESR, photothermal deflection spectra (PDS) and Raman spectra.

[1] T. Iwasaki, M. Aono, S. Nitta, H. Habuchi, T. Itoh and S. Nonomura, Diamond and Related Materials 8 (1999) 440.

[2] S. Nitta, N. Takada, K. Sugiyama, T. Itoh and S. Nonomura, J. Non-Cryst. Solids 227-230 (1998) 655.

[3] N. Takada, K. Arai, S. Nitta and S. Nonomura, Applied Surface Science 113/114 (1997)

4:45 PM U12.10

OBSERVATION OF BLUE EMISSION FROM ECR-CVD DEPOSITED AMORPHOUS HYDROGENATED SILICON CARBIDE. J. Cui, Rusli, S.F. Yoon, M.B. Yu, K. Chew, J. Ahn and Q. Zhang, School of Electrical and Electronic Engineering, Nanyang Technological University, SINGAPORE.

Hydrogenated amorphous silicon carbide (a-SiC:H) thin films have attracted considerable interests due to their unique properties such as wide and tunable bandgap, chemical inertness and potential applications in electronics and optical devices including solar cells, image sensors, and thin film light emission diode. In this work, we report on a-SiC:H films deposited by the electron cyclotron resonance chemical vapour deposition (ECR-CVD) technique, which has so far not been widely investigated for the growth of a-SiC:H. This technique has advantages such as high ion density and high electron temperature, and has been shown to lead to films with low defect density. Silane (10% diluted in hydrogen), methane and hydrogen were used as source gases with the corresponding flow rates of 10, 2 and 100sccm. The microwave power was varied from 100W to 1000W with the deposition pressure and substrate temperature kept constant at 22mT and 20°C respectively. The optical bandgap E₀₄ was found to decrease from 3.54 to 3.08eV with increasing microwave power from 100W to 600W, beyond which the E₀₄ increases again. Upon excitation using 363.8nm line from an Ar⁺ ion laser, visible single broad band PL can be clearly seen by naked eyes for all the samples deposited. The peak emission energy increases with the bandgap and ranges from 2.44 to 2.79eV. The dependence of the PL FWHM on the disorders indicated by the Urbach tail width E₀ and B factor of the Tauc plot will also be investigated together with the structural properties of the films. The strong hydrogen dilution coupled with the ECR plasma is believed to result in higher bandgap a-SiC:H films with lower defect density, and hence blue PL emission. The results obtained are significant in terms of realizing the potential applications of a-SiC:H in large area flat panel displays.