

SYMPOSIUM T

Nanostructured Diamond and Diamond-Like Materials for Micro- and Nanodevices

March 31 - April 1, 2005

Chairs

Orlando Auciello

Materials Science Division
Argonne National Laboratory
9700 S. Cass Ave.
Argonne, IL 60439
630-252-1685

John A. Carlisle

Materials Science Division
Argonne National Laboratory
Bldg. 200/D169
9700 S. Cass Ave.
Argonne, IL 60439
630-252-3520

Robert J. Nemanich

Dept. of Physics
North Carolina State University
Raleigh, NC 27695-8202
919-515-3225

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* Invited paper

8:30 AM *T1.1

Tetrahedral Amorphous-Carbon MEMS – Processing and Properties. Thomas Aquinas Friedmann¹, Sullivan P. John¹, Dave A. Czaplowski¹, James R. Webster¹, Chris W. Dyck¹, Dustin W. Carr¹, Bianca E. N. Keeler¹, Joel R. Wendt¹, Sung Woo Cho² and Ioannis Chasiotis³; ¹Sandia National Laboratories, Albuquerque, New Mexico; ²Materials Science and Engineering, University of Virginia, Charlottesville, Virginia; ³Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia.

Diamond-like tetrahedral amorphous-carbon (ta-C) thin films have mechanical and tribological properties that make them ideal candidates for micro-electro-mechanical machines (MEMS). Their high hardness, wear resistance, and chemically inert surfaces could allow for more robust devices, especially for the troublesome case of MEMS with contacting surfaces. We have been fabricating simple single-level MEMS from ta-C to study the processing and integration with other materials, and we have been using the fabricated devices to evaluate thin film mechanical and electrical properties. This talk will focus on selected aspects of these studies in order to present an evaluation of the advantages and disadvantages of using ta-C as a MEMS material. Specific processing issues to be addressed include stress control, etching parameters, and adhesion to other MEMS materials. For example, control of in-plane average stresses and out-of-plane stress gradients is a significant issue for ta-C. We have used high temperature annealing and laser annealing to relieve these stresses. We have also used etch-back studies to characterize stress gradients in thermally processed films. We have shown that it is possible to reduce and control stresses to <10 MPa levels by thermal annealing to produce relatively flat released structures. We have also studied ta-C mechanical, dissipative, and electrical properties using fabricated devices. Three examples will be discussed. First, micro-tensile test specimens were fabricated and tested on a custom test apparatus that included an integrated atomic force microscope (AFM) for strain measurement. Second, nanomechanical resonators were fabricated using e-beam lithographic patterning with critical dimensions as small as 0.05 μm and their Q measured to characterize dissipation mechanisms present in ta-C. As a result of these studies a highly sensitive novel optical measurement technique was invented to measure in-plane motion of biased resonators with an in-plane motion sensitivity of <160 fm/Hz^{0.5}. Third, ta-C has been used as the dielectric layer in RF MEMS capacitive switches in order to reduce problems associated with dielectric charging. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy National Nuclear Security Administration under contract DE-AC04-94AL85000. The work at UVA was supported by the Air Force Office of Scientific Research through grant F49620-03-1-0080 and the National Science Foundation under grant CMS-0301584.

9:00 AM T1.2

Growth and Characterization of Nanostructured Diamond and Diamond-Like Carbon in a Low Pressure Inductively Coupled Plasma. Katsuyuki Okada and Shojiro Komatsu; National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

A 13.56 MHz low pressure inductively coupled CH₄/CO/H₂ plasma has been applied to prepare nanocrystalline diamond particles with several hundred nm in average diameter [1,2]. The minimum diameter of the particles was found to be 5 nm. Two-dimensional platelet-like graphite and carbon nanotubes also were deposited with different conditions. The characterizations were performed with transmission electron microscopy (TEM), Raman spectroscopy, and electron energy loss spectroscopy (EELS). The TEM observations have revealed [1] that the two-dimensional platelet-like deposits consist of disordered microcrystalline graphite, whereas the particles are composed of only diamond nanocrystallites. The high-resolution TEM images clearly show that each particle is composed of small particles of about several ten nm in diameter. The X-ray diffraction pattern exhibits the diffraction peaks of diamond (111) and (220) planes. The crystallite size was estimated to be approximately 20 nm from the full width at half maximum (FWHM) of the diamond peaks by using the Scherrer's equation. It is consistent with the TEM observations. The visible and ultraviolet (UV) excited Raman spectra show a peak around 1150 cm⁻¹ derived from nanocrystalline diamond and a peak at 1332 cm⁻¹ assigned to zone center optical phonon mode with F_{2g} symmetry of diamond [3]. The EEL spectrum shows a peak at 290 eV due to (σ)^{*} states and the energy loss near edge structure is similar to that of diamond. A slight peak appears around 285 eV corresponding to (π)^{*} states. The mapping of sp² states by (π)^{*} peak reveals that sp²-bonded carbons are identified around the 20-50 nm sub-grains of

nanocrystalline diamond particles at approximately 1 nm resolution [4]. The low loss region of EEL spectra exhibits a bulk plasmon peak of diamond at 33 eV and a surface plasmon peak of diamond at 23 eV. The diamond particles with several nm in diameter are expected to exhibit an emission in UV region and could be used for an UV-light emitting nanodevice. [1] K. Okada, S. Komatsu, and S. Matsumoto, J. Mater. Res. 14, 578 (1999). [2] K. Okada, Encyclopedia of Nanoscience and Nanotechnology, 8, 691 (2004). [3] K. Okada, H. Kanda, S. Komatsu, and S. Matsumoto, J. Appl. Phys. 88, 1674 (2000). [4] K. Okada, K. Kimoto, S. Komatsu, and S. Matsumoto, J. Appl. Phys. 93, 3120 (2003).

9:15 AM T1.3

Diamond-Like Carbon Films Deposited at Different Substrate Biases using a Saddle Field Fast Atom Beam Source.

Rajnish Sharma¹, Sushil Kumar², P. N. Dixit², O. S. Panwar², P. J. George³, C. M. S. Rauthan², K. M. K. Srivatsa² and R. Bhattacharayya²; ¹EEE Group, Birla Institute of Technology and Science, Pilani, Rajasthan, India; ²Plasma Processed Materials Group, National Physical Laboratory, K.S. Krishnan Marg., New Delhi, Delhi, India; ³Electronic Science Department, Kurukshetra University, Kurukshetra, Haryana, India.

Introduction to the work: Diamond Like Carbon (DLC) films have been researched for last many years since their discovery by Aisenberg and Chabot way back in 1970s. Besides regular applications of these DLC films like in tribology, ophthalmic glasses etc, a thorough research effort is being devoted since last few years to make possible use of these films for making field emission display devices. In this paper, we wish to report the results of our studies carried out on DLC films deposited by relatively novel technique i.e. saddle field Fast atom beam source (FAB). Mainly, effect of substrate bias has been studied while keeping power applied the source at a constant value. Firstly, more regular characterization parameters were studied like deposition rate, film morphology (using XAES and IR), residual stress and hardness etc. After establishing basic results, effort was put on to study the field emission properties of thus deposited DLC films. Along with this experiment, effect of nitrogen dilution was also studied well in depth. Summary of results obtained: Deposition rate was found to decrease up to ~ 100 V applied substrate bias beyond which it increased. The values of stress and hardness were not found to follow any definite trend on the variation of applied substrate bias. Analysis of the IR plot was carried out by comparing the observed peaks with those reported in the literature. For analyzing the derivative XAES spectra, a parameter (D) defined as the distance between the maximum of positive going excursion and the minimum of negative going excursion was calculated. The values of (D) evaluated from XAES data for DLC films were found to be 14.8, 14.5 and 15.2 at V_s = 0V, 90V and 180 V respectively. The sp³ content percentage and sp³/sp² ratio was found to be 94.4 and 16.7, 97.7 and 42.5 at V_s = 0V and 90V respectively. Beyond V_s = 90V these values started decreasing. This typical observation of a point of inflection in the properties of DLC films studied over here at around 90V of applied substrate bias commensurate well with the observation of a dip in the deposition rate plot and the structural predictions from IR. The threshold field (E_{turn ON}) for electron emission showed a minimum at 3.5 V/ micron mts. in DLC films grown with 32 W power applied to the source, which got reduced to 2.7 V/ micron mts, at 100 V of applied substrate bias. Nitrogen dilution of the feedstock (methane) of the order of 27% helped in reduction of (E_{turn ON}) even further to 2.4 V/ micron mts. One line statement about the highlights of present research effort: We have been able to observe a correlation between field emission properties and residual stress of DLC films. In full manuscript, the results obtained like point of inflation and low values of (E_{turn ON}) will be explained by use of a newly developed model for movement of film forming precursors from source to substrates.

9:30 AM T1.4

Nano-Carbon for Tera-Bits. Cinzia Casiraghi, Andrea Carlo Ferrari and John Robertson; Engineering, Cambridge University, Cambridge, United Kingdom.

Diamond-like Carbon (DLC) is the preferred coating material for magnetic storage disks and future optical storage, where developments of DLC as a protective layer could allow increases of the data storage density to ~ 1 Tbit/in² and ~ 100 Gbit/in², respectively. Tetrahedral amorphous carbon (ta-C) films are being used to coat the read heads. Films with a thickness below 2 nm and roughness well below 1 nm are needed to achieve the desired storage densities. To reach these values, we must determine the minimum thickness for continuous and pin-hole free films. Here, we study the smoothness and the growth mechanism of ta-C. The film roughness R of every growing surface generally increases with the thickness z as $R \sim z^\beta$ until reaching saturation [1,2]. For a fixed thickness, R increases with the lateral scale length L as $R \sim L^\alpha$. The exponents α and β are called roughness and growth exponents, respectively, and they are uniquely defined by the growth process [1,2]. The roughness evolution of ta-C films grown

at room temperature was measured by atomic force microscopy. The roughness is very low (~ 0.12 nm) and the growth exponents are $\alpha \sim 0.39$ and $\beta \sim 0.01$ [3]. These low exponents require the presence of surface diffusion and relaxation. We propose that the diffusion is quite local and it occurs during the thermal spike, which accompanies ion dominated depositions. Monte Carlo simulations confirm this and show low exponents consistent with our experiments. Thus, the scaling analysis shows that the surface properties are a separate process to the subplantation, which determines the sp³ bonding of the bulk film. A direct assessment of the absence of pin-holes in ultra-thin ta-C films was performed by X-ray photoelectron spectroscopy and corrosion measurements [4]. These confirm that the minimum thickness for full coverage is not higher than ~ 1 nm for ta-C, in agreement with our dynamic scaling results. Thus ta-C satisfies the requirements for the ultimate storage density of ~ 1 Tbit/in², in contrast with the traditional hard disk coatings. 1. F. Family, *Physica A* 168, 561 (1990). 2. A.L.Barabasi, H.E.Stanley, *Fractal concepts in surface growth*, Cambridge University Press N. York (1995). 3. C. Casiraghi, A. C. Ferrari, R. Ohr, A. J. Flewitt, D. Chu, J. Robertson, *Phys. Rev. Lett.* 91, 226104 (2003) 4. P. Bernhard et al. *Surf. Coat. Tech.* 180-181, 621 (2004)

10:15 AM T1.5

Hybrid Passivation of Polyimide Film on Diamond-Like Carbon Film. F. C. Tai^{1,2}, S. C. Lee¹, Yu Rick² and Tsai Mars²;
¹Material, NCKU, Taiwan, Taiwan; ²Bumping R&D, ASE, Taiwan, Taiwan.

The present study shows the integration of spin-on organic polyimide film used as the upmost film on DLC (Diamond-Like Carbon) film deposited by plasma enhanced chemical vapor deposition method. The thickness of DLC is 1um and the thickness of polyimide is 5um, respectively. There are two critical factors for PI/DLC hybrid film; the first factor is thermal stability of DLC, It is necessary to find out the curing condition for PI/DLC under taking into consideration to get suitable curing degree of polyimide and to avoid the thermal instability of DLC. Raman spectra shows that the DLC begin to degrade at 300C during annealing treatment and FTIR spectra also exhibits that the polyimide can reach 95% curing degree during the 300C thermal treatment. The second factor is the adhesion at PI/DLC hybrid coating, it is fortuned that the DLC film exists the residual compressive stress and polyimide film owns the residual tensile stress, so the polyimide film has the potential ability to release partially the residual compressive stress of DLC film at PI/DLC hybrid film. Wafer warpage measurement shows that polyimide film with 0.09GPa tensile stress can be used as stress buffer layer on DLC film with 1.82GPa maximum compressive stress. Tape test results shows that there is no visual peeling phenomena at the PI/DLC or DLC/Si interface. The results obtained so far show that the integration of PI with DLC hybrid film as integral passivation layer is possible, because DLC film has been used as the low-k interlayer dielectric film and PI film also has been used as the passivation film in manufacturing process of IC device.

10:30 AM T1.6

The Substrate Effect on the Mechanical Properties of Diamond Like Carbon Films under Different Film Thickness. Cheung Wei and Ping-Chi Chiang; Mechanical Engineering, Tatung University, Taipei, Taiwan.

The good properties of diamond-like carbon (DLC) film like high hardness, low friction coefficient, resistance to chemical corrosion and good biocompatibility make it an excellent material in many applications. As the films thickness grows smaller, the precise evaluation of mechanical properties has become a challenge. To understand the substrate effect in measuring the material properties of DLC films, we employ nanoindentation to study Young's modulus and hardness for different film thickness from 44 nm to 826 nm on silicon and glass substrate. The microstructure of the films was examined by Raman spectroscopy and the indentation profile was taken by atomic force microscopy. The experimental results show that Young's modulus and hardness has greater variation in small film thickness and the substrate effect is prominent in this film thickness range. As the film thickness is larger, the Young's modulus and the hardness on different substrates show similar values. The correlation between the mechanical properties and the composition was examined by G band position in Raman spectroscopy. The trend of the slope change of the G band position was similar to that in Young's modulus but not in hardness. The atomic structure seems correlated with Young's modulus. The different nature in elastic modulus and hardness might be the reason.

10:45 AM T1.7

Anomalous Current-Voltage Characteristics, Colossal Electroresistance and Colossal Magnetoresistance of Doped Amorphous Carbon Film on Si Substrate. Xiaozhong Zhang, Q. Z. Xue, G. T. Tan and P. Tian; Materials Science and Engineering,

Tsinghua University, Beijing, China.

Amorphous carbon (a-C) films are deposited on Si substrates at different temperatures using pulsed laser deposition (PLD). Some anomalous current-voltage (I-V) characteristics of the a-C films/Si are reported. The a-C films/Si deposited at 27 degree C has an apparent voltage-induced switch effect, and the value of the switch voltage decreases with increasing temperature. The colossal electroresistance (ER) of -84.5% was achieved at T=310K. However, the I-V characteristics of the a-C films/Si deposited at 300 degree C and 500 degree C are completely different from that of a-C films/Si deposited at 27 degree C. It is also found that the resistance of Fex-C1-x films on Si (100) substrates are controlled by the measuring current within a given temperature range so that the films have unusual asymmetric I-V curves. Correspondingly, colossal electroresistance (ER) and colossal magnetoresistance (MR) were found in this materials. For example, Fe0.011-C0.989 film has a positive colossal MR of 138% at temperature of 300K and magnetic field of 5T. It is found that the switching of the conducting channel from the Fex-C1-x film to the Si substrate plays an important role in the current-dependent resistance of Fex-C1-x films. The easy control of the resistance of Fex-C1-x film by electric current should be of interest for various applications such as field-effect devices. The multilayer of Fex-C1-x films on Si (100) substrate was prepared by PLD. This multiplayer material has a positive colossal MR of over 30% at magnetic field of 0.01T, which is comparable to the spin-valve structure of traditional giant magnetoresistance (GMR) materials. However, its MR mechanism can not be explained by GMR or ordinary magnetoresistance (OMR), showing that the material has a novel MR mechanism. It is believed that this multiplayer material can find application in magnetic information storage such as magnetic sensors, magnetic recording head and magnetic random access memory (MRAM).

11:00 AM *T1.8

Connecting Nanotribology with the Surface Chemistry and Structure of Ultrananocrystalline Diamond and Tetrahedral Amorphous Carbon Thin Films. Robert W. Carpick¹, Anirudha V. Sumant¹, David S. Grierson¹, Guoqing Ning¹, James D. Birrell², Jennifer E. Gerbi², John A. Carlisle², Orlando Auciello² and Thomas A. Friedmann³; ¹Engineering Physics, University of Wisconsin - Madison, Madison, Wisconsin; ²Argonne National Laboratories, Argonne, Illinois; ³Sandia National Laboratories, Albuquerque, New Mexico.

The atomic structure and bonding at surfaces have a dramatic effect on friction, adhesion, and wear at the nanometer scale, and therefore they need to be carefully considered when trying to understand the fundamental nature of friction, and its impact in a range of applications, including micro- and nano-electromechanical systems, where tribological failures are critical. We are studying two novel forms of ultrahard carbon films: ultrananocrystalline diamond (UNCD) and tetrahedral amorphous carbon (ta-C). The surface and near-surface chemistry and bonding structure of these films are examined using synchrotron-based near-edge X-ray absorption fine structure spectroscopy, which is a powerful technique for examining the amount of pi- and sigma-bonded carbon and other local bonding properties. Using quantitative atomic force microscopy, we measure nano-scale adhesion and friction of the tribologically relevant underside of the films. In addition to being far less adhesive than a silicon reference sample, UNCD can be processed to render it chemically identical to single crystal diamond, minimizing the work of adhesion to the van der Waals limit and strongly reducing friction as well. With ta-C, we present nanotribological measurements for ta-C-coated AFM tips in contact with ta-C surfaces, and discuss how film annealing processes alter both the bonding in the film and the nanotribological response. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC02-94AT85000.

SESSION T2: Synthesis, Properties and Characterization of NCD Films
 Chairs: James Birrell and Horacio Espinosa
 Thursday Afternoon, March 31, 2005
 Room 3022 (Moscone West)

1:30 PM *T2.1

A Comparison of Mechanical Properties of Three MEMS Materials - Silicon Carbide, Ultrananocrystalline Diamond, and Hydrogen-Free Tetrahedral Amorphous Carbon (Ta-C). H. D. Espinosa¹, B. Peng¹, N. Moldovan¹, T. A. Friedmann², X. Xiao³, D. C. Mancini³, O. Auciello³, J. Carlisle³ and C. A. Zorman⁴;
¹Mechanical Engineering Department, Northwestern University, Evanston, Illinois; ²Sandia National Laboratories, Albuquerque, New Mexico; ³Argonne National Laboratory, Argonne, Illinois; ⁴Case

Many MEMS devices are based on polysilicon because of the current availability of surface micromachining technology. However, polysilicon is not the best choice for devices where extensive sliding and/or thermal fields are applied due to its chemical, mechanical and tribological properties. In this work, we investigated the mechanical properties of three new materials for MEMS/NEMS devices: silicon carbide (SiC) from Case Western Reserve University (CWRU), ultrananocrystalline diamond (UNCD) from Argonne National Laboratory (ANL), and hydrogen-free tetrahedral amorphous carbon (ta-C) from Sandia National Laboratories (SNL). Young's modulus, strength, fracture toughness, and theoretical strength were measured for these three materials using only one testing methodology - the Membrane Deflection Experiment (MDE) developed at Northwestern University. The measured values of Young's modulus were 430GPa, 960GPa, and 800GPa for SiC, UNCD, and ta-C, respectively. Fracture toughness measurements resulted in values of 3.2, 4.5, and 6.2 MPa \times m^{1/2}, respectively. The strengths were found to follow a Weibull distribution but their scaling was found to be controlled by different specimen size parameters. Therefore, a cross comparison of the strengths is not fully meaningful. We instead propose to compare their theoretical strengths as determined by employing Novozhilov fracture criterion. The estimated theoretical strength for SiC is 10.6GPa at a characteristic length of 58nm, for UNCD is 18.6GPa at a characteristic length of 37nm, and for ta-C is 25.4GPa at a characteristic length of 38nm. The techniques used to obtain these results as well as microscopic fractographic analyses will be discussed. We also highlight the importance of characterizing mechanical properties of MEMS materials by means of only one simple and accurate experimental technique. Keywords: MEMS materials, mechanical testing, strength, fracture toughness. Author to whom correspondence should be addressed, espinosa@northwestern.edu This work was supported by the DOE-Office of Science-Materials Science under Contract No. W-31-109-ENG-38, and NSF-NIRT grant.

2:00 PM T2.2

Nanotribology of Boron-Doped and Undoped Nanostructured Diamond Films on Titanium Alloy. Qi Liang, Shane Aaron Catledge, Andreiy Stanishkevsky and Yogesh K. Vohra; Physics, University of Alabama at Birmingham, Birmingham, Alabama.

Nanostructured boron-doped and undoped diamond films were deposited on mirror polished Ti-6Al-4V substrates at 800 °C in a microwave plasma assisted CVD system. Sliding tests were conducted in ambient air with a CSM nanotribo-meter operated in linear motion mode. The sliding counterface was a 3 μ m thick nanostructured diamond film that was CVD-coated onto a 2.5 mm diameter sphere of Ti-6Al-4V. The tribological results and examination of the coatings shows that smooth diamond coatings demonstrate extremely low coefficient of friction and wear rate as compared to commonly used uncoated materials such like mirror polished Ti-6Al-4V and Co-Mo-Cr alloy. A systematic study on the relation between applied normal load and coefficient of friction for both undoped and boron doped nanostructured diamond was carried out. It was found that because of its relatively larger grain size and higher surface roughness, the coefficient of friction for boron doped nanostructured diamond films is generally higher than undoped nanostructured diamond films. It was also found that for undoped nanostructured diamond films, an exponential decay in first order can be used to fit the coefficient of friction as a function of applied normal load, with a measured coefficient of friction as low as 0.017. The wear rate for both undoped and boron doped nanostructured diamond films linearly increases with increased normal load, and the wear rate of boron doped nanostructured diamond films is higher than undoped films. Under low normal load and stress (60mN, 1.23GPa) the wear rate for undoped nanostructured diamond film is as low as 5.2 x 10⁻⁹ mm³/Nm, which is comparable to that of polished polycrystalline diamond. No surface deformation, film delamination or micro-cracking was observed for undoped nanostructured diamond films. However, the boron doped nanostructured diamond films exhibited surface deformation above a critical failure stress 2.2 GPa. Overall, our results show that nanostructured diamond coatings may be a very important route for improving the wear and friction properties of Ti-6Al-4V. Our previous research has shown that boron doped nanostructured diamond film can improve the open air thermal stability of nanostructured diamond films by 100 C°. Boron doped nanostructured diamond films will have potential applications in wear resistant coatings at the operating temperature up to 700 C°. Authors acknowledge support from the National Institute of Dental and Craniofacial Research (NIDCR) under Grant No. R01 DE013952-04.

2:15 PM T2.3

Diamond Film Synthesis at Substrate Temperatures sub 400 C. Fabrice Piazza¹, Vladimir Makarov¹, Rafael Velazquez¹, Joel De Jesus¹ and Gerardo Morell^{1,2}; ¹Department of Physics, University of

Two issues hamper the utilization of the outstanding properties of microcrystalline diamond in microelectronics: no electronic-grade n-type semiconducting diamond has been produced so far with good reproducibility, and most of the current growth processes are carried out at too high substrate temperature, typically higher than 700 C. Electronic-grade n-type semiconducting diamond film deposition at lower substrate temperature is therefore of considerable interest. We recently succeeded in making n-type diamond by sulfur doping [S. Gupta, B.R. Weiner, G. Morell, Applied Physics Letters 83, 491, 2003]. The films were grown by hot-filament chemical vapor deposition (HFCVD) from CH₄/H₂ gas mixture and trace amounts of sulfur, in the form of hydrogen sulphide (H₂S), at substrate temperature around 700 C. We were then able to produce high-quality microcrystalline diamond (micro-D) and nanocrystalline diamond (nano-D) at substrate temperature as low as 440 C, on temperature sensitive materials of industrial interest [F. Piazza, J.A. Gonzalez, R. Velazquez, J. De Jesus, S.A. Rosario, G. Morell, Diamond Relat. Mater., submitted]. We now report on the growth of high-quality micro-D and nano-D films by sulfur-assisted HFCVD at substrate temperature lower than 400 C. The result is interpreted in terms of profound changes in the gas phase chemistry in presence of sulfur in the form of H₂S, as observed by laser cavity ring-down absorption spectroscopy. The effects of substrate temperature in presence of sulfur on diamond growth and structure are investigated using scanning electron microscopy, atomic force microscopy, X-ray diffraction analysis, X-ray photoelectron spectroscopy, Auger electron spectroscopy, and visible and UV Raman spectroscopy.

2:30 PM T2.4

Smooth, Low-Stress and Ultra-thick Nanocrystalline Diamond Films. Joseph W. Tringe¹, Juergen Biener¹, Yinmin Wang¹, Sergei O. Kucheyev¹, Paul B. Mirkarimi¹, Alex V. Hamza¹ and Kai Bruehne²; ¹Nanoscale Synthesis and Characterization Laboratory, Lawrence Livermore National Laboratory, Livermore, California; ²Ingenieurwissenschaften, Abt. Werkstoffe der Elektrotechnik, Universitaet Ulm, Ulm, Germany.

Diamond films prepared by chemical vapor deposition (CVD) are commonly used as mechanically hard coatings. The roughness of polycrystalline diamond films typically increases with the film thickness and is usually on the order of 20-30% of the film thickness. Friction caused by the large surface roughness of thicker diamond films presents a major obstacle for some applications such as diamond cog wheels in microelectromechanical systems (MEMS). Diamond films with a nanocrystalline grain structure, by contrast, exhibit much smoother surfaces. However, the applicability of these films is often hampered by the presence of high internal stress. Here, we present results on the characterization of an ~ 90 micron thick nanocrystalline diamond film with low internal stresses. The material was prepared by hot filament-assisted CVD using a mixture of methane, oxygen, and hydrogen. The film exhibits a surface roughness at the sub-micron level on a mm length scale, which is considerably smoother than the typical roughness of coarse-grained material of comparable thickness. The film structure was studied by cross-sectional transmission electron microscopy (TEM), as well as Raman and IR spectroscopies. In addition, Rutherford backscattering spectrometry and synchrotron-based X-ray absorption spectroscopy were employed to analyze the chemical composition, and nanoindentation was used to evaluate mechanical properties. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract of No.W-7405-Eng-48.

3:15 PM *T2.5

The Potential of Carbon Based Materials in Vacuum Thermionic Energy Conversion. Franz A. Koeck¹, Joshua R. Smith¹, Jacob Garguilo¹, Yunyu Wang¹, Sanju Gupta², Griff Bilbro³ and Robert J. Nemanich¹; ¹Department of Physics, North Carolina State University, Raleigh, North Carolina; ²Department of Physics, Astronomy, and Materials Science, Southwest Missouri State University, Springfield, Missouri; ³Department of Electrical and Computer Engineering, North Carolina State University, Raleigh, North Carolina.

Thermionic energy conversion is a process where thermal energy is transformed into electricity by utilizing an electron emitter held at an elevated temperature separated from a cooler collector by a vacuum gap. Conventional thermionic energy converters were designed with flat, metal based electron emitters and required high operating temperatures. In addition, these flat emitters were limited by space charge effects. Carbon based materials, i.e. doped and nanostructured diamond and carbon nanotube films exhibit unique emission characteristics which can be exploited for electron emitters in a thermionic converter configuration. Emission from doped diamond

films is dominated by thermionic effects starting at $\sim 600^\circ\text{C}$ with a strong increase in emission with temperature. This emission is uniform over the surface in contrast to nanostructured carbon films where localized emission sites are observed. Localized emission, in general, is attributed to a non uniform distribution of the field enhancement across the surface of the emitter. Field enhancement based emitters can reduce space charge effects by providing means of efficient carrier release into the vacuum gap. Sulfur doped nanocrystalline diamond as well as carbon nanotube films exhibit strong temperature dependence in the emission characteristics and are also characterized by low emission threshold fields. These emission parameters describe emitter materials which are promising for efficient thermionic energy converters operating at temperatures $< 1000^\circ\text{C}$. This research is supported by the TEC-MURI project.

3:45 PM *T2.6

Adjustable Properties of Ultrananocrystalline Diamond Thin Films. James Birrell¹, X. Xiao², O. Auciello², J. A. Carlisle² and J. E. Gerbi³; ¹Advanced Diamond Technology, Champaign, Illinois; ²Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ³Department of Materials Science & Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Carbon materials exhibit a wide variety of forms with a broad range of material properties. In particular, diamond has a number of properties that are attractive for numerous applications to macro, micro, and nanodevices. One way to increase the utility of diamond thin films is to tailor its microstructure, particularly reducing the grain size to the nanometer scale, which provide diamond thin films with a unique combination of mechanical, tribological, electron and thermal transport, electrochemical, and biocompatible properties. Specifically, ultrananocrystalline diamond (UNCD) thin films exhibit a wide variety of properties based on both the inherent traits of diamond and some properties inherent of crystalline films with grain sizes between 3 - 8nm. This talk will cover a discussion of many of the tunable materials properties found in UNCD along with the structural changes that enable the unique combination of materials properties described above, including exploring the transition from microcrystalline diamond to a nanocrystalline film structure, "doping" UNCD with nitrogen in order to get semimetallic conduction, growth of UNCD thin films at low temperatures, the role of hydrogen in UNCD thin film growth and properties, as well as the applications apparent for each of these adjustable parameters present for UNCD thin film growth. This work was supported by the DOE-Office of Science-Materials Science under Contract No. W-31-109-ENG-38.

4:15 PM T2.7

Cavity Ring Down Spectroscopy of C2 in Nanocrystalline Diamond Forming Plasmas. Phillip John^{1,2}, James R. Rabeau^{1,2} and John I. B. Wilson¹; ¹School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, United Kingdom; ²Department of Physics, University of Melbourne, Melbourne, Victoria, Australia.

Cavity ring down spectroscopy (CRDS) of the C2 radical has been performed in diamond forming hydrogen-methane-inert gas microwave plasmas [1]. The formation of nanocrystalline diamond was studied in two types of 2.45GHz reactor: antennae type UHV multi-mode reactor and a newly developed coaxial blade (CBR) reactor. The absorption spectrum of the C2 ($d3\pi_g - a3\pi_u$) Swan band [2] was used to measure rotational temperatures and absolute number densities in H₂/CH₄/(He or Ar) plasmas. Optical emission spectroscopy (OES) was monitored for the same optically allowed transition and the electron temperatures measured by the relative H_a and H_b emission intensities. Nanocrystalline diamond films, grown on silicon, were characterised by SEM, AFM, Raman and TEM. Growth rates, crystallite size, film morphology and sp³/sp² ratios were determined as a function of the gas composition. The dependence of the film properties on the plasma parameters and properties, specifically the dependence on the C2 concentration, was examined. The results of this study do not point to C2 as the predominant growth species in the microwave plasma deposition of nanocrystalline diamond. References 1. JR Rabeau, PhD Thesis, Heriot-Watt University 2003. 2. P John, JR Rabeau and JIB Wilson, Diamond and Related Mater.,11 (2002) 608.

4:30 PM T2.8

Field Emission Properties Carbon Nanotubes Grown on Sulfur-Doped Nanocrystalline Diamond Films. Kishore Uppireddi, Fabrice Piazza and Gerardo Morell; Physics, University of Puerto Rico, San Juan, PR, Puerto Rico.

Electron field emission (EFE) properties of carbon nanotubes (CNTs) grown on sulfur-doped nanocrystalline diamond (n-D:S) films were investigated. These two materials show excellent EFE properties separately. The CNTs and the sulfur-doped nanocrystalline diamond films were synthesized in the same hot filament chemical vapor deposition (HFCVD) system at relatively low methane concentrations.

The effects of growth process parameters of CNTs and sulfur incorporation in the nanocrystalline diamond films on the field emission properties were studied. Their morphology and structure were characterized by SEM, energy-filtered TEM and Raman spectroscopy. The amount of sulfur incorporated in the films was quantified from EDX and XPS techniques. The dependence of EFE properties on film composition and morphology is discussed.

4:45 PM T2.9

X-ray Absorption and Emission Studies of Diamond Nanoparticles. Tony van Buuren¹, Christoph Bostedt², Trevor M. Willey¹, J. Y. Raty³, G. Galli¹ and L. J. Terminello¹; ¹Lawrence Livermore National Laboratory, Livermore, California; ²Institute for Atomic Physics, Technical University, Berlin, Germany; ³University of Liege, Liege, Belgium.

Carbon nanoparticles, produced in detonations, are found to have a core of diamond with a coating of fullerene-like carbon. X-ray diffraction and TEM show that the nanodiamonds are crystalline and approximately 4 nm in diameter. These nano-sized diamonds do not display the characteristic property of other group IV nanoparticles: a strong widening of the energy gap between the conduction and valence bands owing to quantum-confinement effects. For nano-sized diamond with a size distribution of 4 nm, there is no shift of the band energies relative to bulk diamond[1]. The C 1s core exciton feature clearly observed in the K-edge absorption of bulk diamond is attenuated and broadened in the nanodiamond case due to increased overlap of the excited electron with the core hole in the small particle. Also the depth of the second gap in the nanodiamond spectra is shallower than that of bulk diamond. A feature at lower energy in the X-ray absorption spectra that is not present in the bulk samples is consistent with a fullerene like surface reconstruction. Electronic structure of the interior and surface of individual diamond nanoparticles were measured by high spatial resolution TEM-EELS. These measurements show the core of the particle is bulk diamond like whereas the surface has a fullerene like structure. Density-functional theory calculations on clusters show an increase in bandgap only for clusters smaller than 1 nm, and confirm the fullerene-like surface reconstruction. This work is supported by the U.S. DOE, BES Materials Sciences under contract W-7405-ENG-48, LLNL. [1] J. Y. Raty, G. Galli, C. Bostedt, T. van Buuren, L. J. Terminello, Phys. Rev. Lett. 90, p.401 (2003) .

SESSION T3: Poster Session:
Thursday Evening, March 31, 2005
8:00 PM
Salons 8-15 (Marriott)

T3.1

Diamond MISFET on Homoepitaxially Grown B-doped (100) and (111) Substrates. Takeyasu Saito¹, Masahiko Ogura¹, Kyung-ho Park¹, Kazuyuki Hirama², Hitoshi Umezawa², Mitsuya Satoh², Hiroshi Kawarada² and Hideyo Okushi¹; ¹Diamond Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; ²School of Science and Engineering, Waseda University, Shinjyuku-ku, Japan.

Diamond semiconductor devices are expected to be of importance for high power and high frequency applications based on its excellent properties. In this decade, low resistive surface conductive layer utilized diamond devices have been focused on due to difficulty in fabrication of low resistive p-type or n-type semiconductive diamond. In addition, homoepitaxial diamond growth studies so far were concentrated on the (100) oriented surface due to availability of both substrate and its smooth surface morphology. The majority of research on diamond devices as MESFET and MISFET on H-terminated surface have also been investigated on (100) substrates, and the cut-off frequency over 20 GHz was achieved. On the other hand, limited number of devices characteristics on H-terminated (111) surface were reported. In this study, the p-type surface conductive layer of B-doped diamond for both (111) and (100) orientation were employed to fabricate MISFET, which utilizes H terminated surface channel and underlying B-doped layer as the major current conductive paths. In the MISFET fabrication processes, Au evaporation on H-terminated region was employed as the source and the drain. Inductively coupled plasma etching process was used for the isolation procedures. Self-aligned gate formation processes with 1-4um gate length were carried out by employing CaF₂ and Cu stacked GOI structures. Orthodox mobility and surface carrier concentration of hydrogenated surface on (100) before FET processing were about 110cm²/Vs and 1E+13/cm², respectively, in where the same properties for (111) substrates were 30cm²/Vs and 1E+13/cm², respectively. The carrier mobility on (111) surface acquired in this study was found to show clear dependency on CH₄/H₂ concentration from 0.1% to 1.5%. This value was still a quarter of that obtained on (100) samples. The DC characteristics of 1um gate length and 50um gate width showed that maximum measured drain current was

190mA/mm on (100) and 240mA/mm on (111) at -3.0V gate voltage, respectively. Based on these values, the maximum transconductance (gm) were 65mS/mm on (100) and 85mS/mm on (111), respectively, however, the reason for better transconductance on (111) is not clear at this moment. The cut-off frequency as 4GHz was obtained from the devices on (111) substrate samples and this is one of the best number for the RF characteristics from diamond homoepitaxial (111) MISFET. In summary, diamond MISFET on B-doped (100) and (111) surface was fabricated, and the maximum drain current and transconductance as 240mA/mm and 85mS/mm, respectively, were obtained from devices on (111) surface. This exhibited the cut-off frequency as 4GHz, which is one of the best value among (111) derived diamond FET to date.

T3.2
Implantation Enhanced Etching of CVD Diamond Studied by Micro-Photoluminescence. P. W. Leech¹, T. Perova², R. A. Moore², G. K. Reeves³, A. S. Holland³ and M. C. Ridgway⁴;
¹Manufacturing and Infrastructure Technology, CSIRO, Clayton South, Victoria, Australia; ²Department of Electronic and Electrical Engineering, University of Dublin, Trinity College, Dublin, Ireland; ³School of Computer Systems and Electrical Engineering, RMIT University, Melbourne, Victoria, Australia; ⁴Electronic Materials Engineering, Australian National University, Canberra, Australian Capital Territory, Australia.

The development of new components in diamond requires a fabrication technique with a suitably high etch rate and the capability of fine patterning. This work has examined the implantation of diamond films as a novel means of increasing the subsequent etch rate. The microcrystalline films of diamond were implanted with ions of widely differing mass (C⁺, Sn⁺ or Si⁺) over a range of dose. For each ion species, a multiple energy implant was used in order to produce a uniform region of vacancy production or disorder. Micro-photoluminescence measurements have examined the induced damage in the diamond as a function of the implant species and dose. The spectra have shown a broad band at 500-750 nm which was attributed to the recombination of donor-acceptor pairs. This feature was related to a rise in the concentration of sp²-bonded carbon located within the grains with increase in the implant dose. For implantation with Sn⁺ or Si⁺ or Sn⁺ ions, a complete amorphisation near to the surface was evident at a dose of 5 x 10¹³ ions/cm². The rate of reactive ion etching of the diamond was measured in CHF₃/O₂, CF₄/CHF₃ and O₂ plasmas. These gas mixtures were previously shown to etch CVD diamond at a relatively slow to moderate rate [1]. The etch rate of the diamond film increased with mass of the implanted ion and with dose. Both of these effects on the etch rate were related to a more basic parameter, the average vacancy production. The etch rate increased directly in proportion to the average vacancy production in the implanted diamond. [1] P.W. Leech, G.K. Reeves and A.S. Holland, J. Mater. Sci. 36, 3453 (2001).

T3.3
Nitrogen-Doped Nanocrystalline Diamond Films Modified with Conductive Polymer for DNA Hybridization Analysis. Zhengqing Xu², Arun Kumar¹ and Ashok Kumar^{2,1}; ¹Nanomaterial and Nanomanufacturing Research Center, University of South Florida, Tampa, Florida; ²Department of Mechanical Engineering, University of South Florida, Tampa, Florida.

Diamond is an ideal platform for biochips because of its superior mechanical, thermal, chemical and electrical properties. In this paper, we study the immobilization of DNA on the conductive polymer modified nitrogen-doped nanocrystalline diamond (NCD) thin films for DNA hybridization analysis. The NCD films are grown on silicon substrate by microwave plasma enhanced chemical vapor deposition (MPECVD). The NCD films are doped by adding nitrogen gas to reactants during the deposition to make the film conductive. A thin layer of conductive polymer film has been electrochemically grown onto the diamond surface. The carboxylic acid residues in the polymer film act as the binding sites for DNA attachment, the conductive polymer enhanced the electron transfer between DNA and the diamond surface. The immobilization of the DNA and the following target hybridization are monitored by electrochemical measurement and FTIR Spectroscopy (Fourier Transform Infrared). This approach could make conductive polymer modified nanocrystalline diamond films as a stable and highly selective platform for DNA hybridization sensing

T3.4
Ultradispersed Nano-Diamond Seeds for Nanocrystalline Diamond Film Synthesis. Rafael Velazquez, Joel De Jesus, Fabrice Piazza and Gerardo Morell; Dept of Physics, University of Puerto Rico, San Juan, Puerto Rico.

The early CVD growth stages are critical for the adhesion and final structure of diamond films. We report on the effect of substrate

seeding with ultra dispersed nano-diamond seeds on the growth and structure of hot filament chemical vapor deposited nanocrystalline diamond. Detonation ultra-dispersed nano-diamond powders were used to seed molybdenum and silicon substrates. For each powder, diamond thin films were grown for 1, 5, 10 and 20 hours. Raman spectroscopy, atomic force microscopy, X-ray photoelectron spectroscopy, and X-ray diffraction analysis were performed to study the growth and structure. The effect of the seeding on the nucleation process, film nanostructure and diamond quality is discussed. Although the films remain highly strained at the nanoscale, as evidenced from the Raman spectra, they can be grown to large thickness values without compromising the substrate adhesion. Thermal shock tests were employed to assess ability of these films to differentially expand and contract while remaining firmly attached to the substrate. These results are discussed in terms of the formation of a thin strong disordered carbide buffer layer at the substrate-film interface capable to adjust and accommodate dynamically any lattice mismatch.

T3.5
Diamond UV Sensors. Iris Monica Vargas¹, Javier Wu¹, Fabrice Piazza¹, Antonio Martinez¹ and Gerardo Morell²; ¹Department of Physics, University of Puerto Rico - Rio Piedras, San Juan, Puerto Rico; ²Department of Physical Science, University of Puerto Rico - Rio Piedras, San Juan, Puerto Rico.

Chemical Vapor Deposition (CVD) polycrystalline diamond is a promising material for ultraviolet (UV) sensors because of its high band gap and carrier mobility, radiation hardness, chemical inertness, high thermal conductivity, and small thermal expansion coefficient. We report on the development of UV sensor using polycrystalline diamond thin film grown by hot-filament chemical vapor deposition (HFCVD). We have been able to decrease the response time and increase the sensitivity of the sensor by controlling the impurity levels, decreasing the film roughness (down to 20-50 nm rms roughness) and fabricating interdigitated metallic structures on them with electrode spacing in the nanometer range using electron-beam lithography. The devices produced show high levels of discrimination between UV and visible radiation.

T3.6
Five Micron Diamond Particles Synthesized in Ten Seconds. Yoshiki Takagi¹, Takayuki Hirai¹ and Tohru Kawai¹; ¹Environmental & Material Engineering, Teikyo University of Science & Technology, Kitatsuru-gun, Yamanashi-pref., Japan; ²Mitsubishi Pencil, Fujioka, Gunma-pref., Japan.

Here we report the new technology of synthesis for diamond particles with five micrometers in diameter in ten seconds with conventional spark apparatus, which originally designed for non-conductive sample pre-treatment for SEM analysis. With these spark apparatus, specimens were coated with carbon fine particles in around ten seconds, and surfaces were kept in low temperature. But carbon fine particles were spread over all directions. The apparatus was specially modified for this study such as tubing for hydrogen gas introduction, with specially designed top shaped rod with prepared ultra-high purity of graphite. We confirmed that diamond particles were synthesized on silicon wafers, Al₂O₃ ceramics and non-alkaline glass. The depositions were performed with conventional spark apparatus (JEOL, JEE-5B), with the chamber sized 200mm in radius and 250mm in height. For synthesize diamond particles, we installed additional tubing for hydrogen gas. We used two graphite rods, one with straight cut shaped and other with sharpened just like screwdriver top. With this shape, we could control the direction of carbon spreading to substrate surface, successfully. Hydrogen gas was installed up to 100 Torr. Silicon wafer substrate was set 5 to 10 mm beneath the rods. Applied electric current was 50A kept in ten seconds. Synthesized particles were observed with SEM and confirmed as diamond with Raman spectrometer. The crystal growth rate with 0.5 micron/second is the highest value ever been reported. The mechanism for this unique reaction method will be presented.

T3.7
Fabrication of Ultrananocrystalline Diamond Probes for Atomic Force Microscopy and Micro-Machining Applications. Ning Guoqing¹, Anirudha V. Sumant¹, David S. Grierson¹, James Birrell², Jennifer E. Gerbi², John A. Carlisle^{2,3}, O. Auciello^{2,3} and Robert W. Carpick¹; ¹Engineering Physics, University of Wisconsin at Madison, Madison, Wisconsin; ²Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ³Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois.

Minimizing wear on tips used in the atomic force microscope (AFM) is a key challenge. Diamond is an ideal candidate material for AFM tips because of its outstanding mechanical, chemical and tribological properties. Unfortunately, it is very difficult to fabricate

atomically-sharp diamond tips with conventional H-rich chemical vapor deposition (CVD) growth techniques due to the large grain sizes (several microns) of the resulting polycrystalline diamond films. However, ultrananocrystalline diamond (UNCD), deposited using Ar-rich CVD, is an ideal candidate material because of its nanoscale grain size (3-5 nm). Here we describe a process to batch-fabricate monolithic UNCD AFM probes. Detailed steps include fabricating pyramidal etch pits on Si wafers by anisotropic etching of Si in KOH followed by UNCD deposition. The UNCD-coated Si wafer then undergoes a series of fabrication steps including metallization, photolithography, and reactive ion etching to form monolithic UNCD cantilevers with an integrated pyramidal tip. These cantilevers are finally released and bonded to a holding piece. We demonstrate the successful fabrication of these probes and initial characterization of their properties. Work at Argonne National Labs was supported by the US Department of Energy, BES-Materials Sciences, under Contract W-13-109-ENG-38.

T3.8
Materials Science and Processing Strategies for Integration of Piezoelectric and Ultrananocrystalline Diamond (UNCD) Thin Films for Piezoactuated Hybrid MEMS. Wei Fan, Goren Bai, J. A. Carlisle and Orlando Auciello; Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

The integration of dissimilar materials and micro and nanofabrication processes need to be investigated and developed to enable a new generation of multifunctional microelectromechanical and nanoelectromechanical system (MEMS/NEMS) devices. Ultrananocrystalline diamond (UNCD) with exceptional mechanical strength, chemical inertness and tribological performance exhibits great potential as a new high-performance material for application to MEMS and NEMS. On a parallel scientific and technological path, ferroelectric/piezoelectric $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) thin films has attracted much attention due to projected applications for intelligent MEMS based on its outstanding piezoelectric and electromechanical coupling coefficients, easy dipole reorientation and high remnant polarization. However, PZT exhibits relatively weak mechanical and tribological properties that hinder its application into MEMS/NEMS devices as a strong microstructural material. Therefore, the opportunity exists for integrating these two dissimilar materials for fabrication of piezoelectrically actuated MEMS/NEMS devices. PZT films need to be grown in O_2 at high temperatures (600-700 °C) on the UNCD layers to achieve the proposed integration. However, growth of PZT, at high temperature in oxygen, on UNCD layers, results in chemical etching of the diamond surface due to formation of volatile CO and or CO_2 species. Another critical challenge lies in the thermal stress between PZT and UNCD that might cause film delamination, following deposition and annealing processes. We demonstrate here that a bi-functional TiAl alloy film can be used as an oxidation barrier and adhesion layer interposed between the PZT and UNCD layers in combination of using conductive metallic or oxide electrode to achieve a successful integration of these two dissimilar materials. Low-temperature thin film growth techniques, including magnetron sputter-deposition for producing the TiAl barrier layer, and MOCVD to produce PZT layers, were used to lower the risk of diamond oxidation. Post-deposition rapid thermal annealing was used to control the crystallography orientation of the PZT layer, thus its piezoelectric properties. The UNCD films were grown by CVD using an Ar-rich CH_4/Ar plasma chemistry. First PZT-films based capacitors with excellent polarization hysteresis loops were produced on UNCD structural layers using the integration described above. Also, processing for producing piezoactuated PZT/UNCD cantilevers will be discussed in view of projected applications to the fabrication of piezoelectrically actuated UNCD-based MEMS/NEMS actuators and sensors. This work was supported by the DOE-Office of Science-Materials Science, under Contract No. W-31-109-ENG-38.

SESSION T4: Characterization of Diamond and Nanocarbon Films

Chairs: R. J. Hamers and B. H. Houston
 Friday Morning, April 1, 2005
 Room 2012 (Moscone West)

8:30 AM *T4.1

In Situ Nanoindentation of Ultrananocrystalline Diamond and Amorphous Diamond Thin Film Coatings. A. M. Minor¹, D. Ge¹, J. W. Morris, Jr.², T. A. Friedmann³, X. Xiao⁴, O. Auciello⁴, J. A. Carlisle⁴ and Eric A. Stach^{1,3}; ¹National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; ²University of California at Berkeley, Berkeley, California; ³Sandia National Laboratories, Albuquerque, New Mexico; ⁴Argonne National Labs, Argonne, Illinois; ⁵School of Materials Engineering, Purdue University, West Lafayette, Indiana.

Ultrananocrystalline diamond (UNCD) and amorphous diamond (a-D) thin films have great potential to be used as surface coatings and as structural layers to fabricate microelectromechanical systems (MEMS) devices in general and biodevices in particular due to their superior mechanical properties, biocompatibility and excellent conformality in the case of UNCD films. Nanoindentation is accepted as the most useful technique to study localized mechanical phenomena in materials of thin film form. However, the mechanisms of deformation can only be inferred from the load-displacement data obtained during a typical instrumented nanoindentation test. In order to elucidate the underlying physics of the mechanical deformation process in these materials, we have utilized the technique of in-situ nanoindentation in a transmission electron microscope (TEM). With this technique, a voltage-actuated piezoceramic tube is used to position a sharp diamond in-plane with the edge of an electron transparent sample. The tip is driven into the material in order to induce deformation and the corresponding response is observed in real time and at high spatial resolution. In this presentation, we will discuss our observations of the indentation of both UNCD and a-D thin films deposited onto bulk micromachined silicon substrates. The use of micromachined substrates to provide electron-transparent samples is critically necessary for the evaluation of these diamond films, since ion-milling converts sp^3 -bonded carbon to sp^2 -bonded. Both thin films show an ideal combination of strength and compliance during elastic loading. The films effectively transfer the load to the substrate without significantly impacting the films themselves. The deformation mechanisms in these films will be discussed and correlated with direct observations and measurements from instrumented indentation tests. This work was supported by the DOE-Office of Science-Materials Science under Contract No. W-31-109-ENG-38.

9:00 AM T4.2

The Electronic Structure of Diamondoids Using Synchrotron Radiation. Trevor M. Willey¹, Christoph Bostedt², J. E. Dahl³, Thomas Moeller², R. M. K. Carlson³, R. W. Meulenbergh¹, E. J. Nelson¹, T. van Buuren¹ and L. J. Terminello¹; ¹Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; ²Institute for Atomic Physics, Technical University, Berlin, Germany; ³Molecular Diamond Technologies, Chevron-Texaco Technology Ventures, Richmond, California.

Although the Group IV semiconductors Si and Ge show quantum confinement effects in nanoparticles, diamond particles a few nanometers in size do not show this increase in band-gap[1]. However, various calculations on diamond predict increasing HOMO-LUMO gap as the diameter decreases below 1 nm[1,2]. We have tested this hypothesis and will present the first measurements of the electronic structure of diamond in this near- and sub- nanometer size regime using synchrotron radiation techniques. Pure, defect-free, hydrogen-terminated diamondoids[3] were investigated in the gas phase to eliminate particle-particle interaction and ensure measurement of pristine molecules. X-ray absorption probes the unoccupied electronic states; the Carbon K-edge reveals rich electronic structure in these materials. We will present our analysis showing the emergence of a diamond-like band structure and a comparison to the predicted change in HOMO-LUMO gap from several calculations and our own recent X-ray absorption and emission measurements on solid-state diamondoids. [1] J. Y. Raty, G. Galli, C. Bostedt, T. van Buuren, L. J. Terminello, Phys. Rev. Lett. 90, 037401 (2003). [2] G. C. McIntosh, M. Yoon, S. Berber, D. Tomanek, Phys. Rev. B 70, 045401 (2004). [3] J. E. Dahl, S. G. Liu, R. M. K. Carlson, Science, 299, 96-99 (2003).

9:15 AM T4.3

Bonding and Structure of Hydrogenated Amorphous Carbons by Resonant Raman Spectroscopy. Cinzia Casiraghi, Andrea Carlo Ferrari, Fabrice Piazza and John Robertson; Engineering, Cambridge University, Cambridge, United Kingdom.

Multi-wavelength Raman spectroscopy has been successfully used to access the structural and the mechanical properties of hydrogen free amorphous carbons [1] and amorphous carbon nitrides [2]. Here we focus on hydrogenated amorphous carbons (a-C:H). We present a comprehensive analysis of the Raman spectra measured at 244 and 514.5 nm of more than 100 hydrogenated amorphous carbon films, grown by different techniques and in different deposition conditions. We show how to analyse the Raman parameters in order to derive the physical properties of these samples. In particular, the sharpness of the G peak directly relates to the amount of order in the samples, which increases going from ta-C:H to polymeric a-C:H. This is reflected in the density and mechanical properties. The G peak dispersion gives further information on the configuration of the sp^2 phase, which is related with the optical properties. The H content can be derived by the photoluminescence background of the visible spectra. The relation between sp^3 content and sp^2 clustering has been investigated as a function of the H content and compared with H free amorphous carbon. The visible Raman spectra alone can give an

indication of the film properties, but a more quantitative analysis can be obtained by combining visible Raman with ellipsometry. For a detailed analysis, multi-wavelength Raman spectroscopy is always recommended. 1. A. C. Ferrari, J. Robertson, *Phys. Rev. B* 61 (2000) 14095; 64 (2001) 075414 2. A. C. Ferrari, S. E. Rodil, J. Robertson, *Phys. Rev. B* 67 (2003) 155306

9:30 AM T4.4

Raman Fingerprint of Fullerene-like Carbons. Cinzia Casiraghi¹, Andrea Carlo Ferrari¹, Jorg Neidhardt², Lars Hultman² and John Robertson¹; ¹Engineering, Cambridge University, Cambridge, United Kingdom; ²Physics, Linkoping University, Linkoping, Sweden.

Nitrogen incorporation into amorphous carbon films can improve their hardness and elastic recovery, especially for films deposited for temperatures higher than 200 C. This happens because nitrogen increases cross-linking between sp² planes, even though not necessarily through an sp³ increase [1,2]. These films are called fullerene-like carbons and are of great technological interest due to their better mechanical and tribological properties. A quick means of detection of fullerene-like carbon films is needed, since so far this is done by high-resolution transmission electron microscopy [3]. Here we show that it is possible to uniquely identify these films by resonant Raman spectroscopy. We consider a set of carbon films deposited by magnetron sputtering for varying substrate bias, nitrogen content and deposition temperature. We identify the optimum set of conditions for fullerene-like carbon growth. These are high temperature (300-500 C) and a nitrogen content of 10-25%. The Raman spectra of fullerene-like carbons shown an increase of the G peak width and G peak dispersion, when nitrogen is introduced in an otherwise graphitic carbon. This results in an increase of disorder and an improvement of the mechanical properties (both Young modulus and elastic recovery). A very different behaviour is seen when N is incorporated into high sp³ carbon films. In these cases nitrogen worsens the Young modulus and increases the fraction of ordered sp² bonds. This again shows uniquely in the Raman spectra as a decrease of the G peak width and G peak dispersion [4]. No feature of a single visible Raman spectrum can be taken as unique signature of fullerene-like carbon bonding. [1] I. Jimenez et al., *Phys. Rev. B* 62, 4261 (2000) [2] W. J. Gammon et al. *Phys. Rev. B* 68, 195401 (2003) [3] J. Neidhardt et al. *J. Appl. Phys.* 93, 3002 (2003) [4] A.C. Ferrari, S. E. Rodil, J. Robertson, *Phys. Rev. B* 67, 155306 (2003).

9:45 AM T4.5

Diffusion Length of Minority Carriers in Sulfur-Doped Microcrystalline and Nanocrystalline Diamond using the Photograting Technique. Fabrice Piazza, Guillermo Nery, Oscar Resto, Luis Fonseca and Gerardo Morell; Physics, University of Puerto Rico, San Juan, PR, Puerto Rico.

Diamond is a promising wide band gap semiconductor with a strong potential for high-power high-temperature electronics. There is also great interest in reproducibly obtaining n-type diamond in connection to applications requiring massive electron transport, especially those involving field electron emission and photoemission, which will be enabled by n-type diamond. We recently succeeded in making n-type diamond by sulfur doping [S. Gupta, B.R. Weiner, G. Morell, *Applied Physics Letters* 83, 491, 2003]. Now we are employing the steady-state photocarrier grating technique to measure the photoconductivity and ambipolar diffusion length of carriers in sulfur-doped microcrystalline diamond (c-D:S) and nanocrystalline diamond (n-D:S) thin films synthesized by hot-filament chemical vapor deposition (HFCVD). The films are grown using methane (CH₄), hydrogen (H₂) and hydrogen sulfide (H₂S) gas feedstocks. The process parameters such as substrate temperature and concentration of hydrogen sulfide are systematically varied while the methane concentration is fixed at 0.3 and 2 % for c-D:S and n-D:S, respectively, to study the corresponding variation on the nanostructure and electronic properties. The nanostructure is analyzed using scanning electron microscopy, atomic force microscopy, X-ray diffraction analysis, X-ray photoelectron spectroscopy, Auger electron spectroscopy, and visible and UV Raman spectroscopy. The results are employed to elucidate the mechanism of n-type conductivity in these sulfur-doped diamond films.

10:30 AM T4.6

Ultrananocrystalline Diamond as a Hermetic, Bio-Inert Coating for Implantable Medical Devices. Xingcheng Xiao¹, Jian Wang¹, John A. Carlisle^{1,4}, Orlando Auciello^{1,4}, Brain Mech², David Zhou², Mark S. Humayun³ and James Weiland³; ¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ²Second Sight, Sylmar, California; ³Doheny Eye Institute, University of South California, Los Angeles, California; ⁴Center for Nanoscaled Materials, Argonne National Laboratory, Argonne, Illinois.

Any implantable device that is to function within the body must not trigger immune reactions or poison the implant environment, i.e. it must be both bio-inert and bio-compatible. In particular, for implants

that are to have silicon-based microelectronic IC chips, a thin-film has yet to be found that renders it suitable for implantation. Silicon and silicon dioxide are both slightly soluble in water, and, for devices that must interact with the biological environment via electrical signals, are subject to hydrolysis and other deleterious electrochemical reactions. It is critical to find a technology that can deposit a film that is $\leq 1 \mu\text{m}$ thick at low temperatures ($< 400^\circ\text{C}$) that is continuous and pin-hole free and whose surface chemistry makes it bio-inert in most biological contexts. In this presentation we will discuss our work to develop ultrananocrystalline diamond (UNCD) thin films as hermetic, mechanically robust, bio-inert/biocompatible coatings. We will discuss the synthesis, microstructural and electrochemical characterization of UNCD coatings grown on high-conductivity Si test substrates in a microwave plasma enhanced chemical vapor deposition (MPECVD) system using an Ar-rich CH₄/Ar/H₂ chemistry. As an example of application of UNCD hermetic coatings, a series of UNCD-coated high-conductivity Si samples were prepared by growing UNCD films with different hydrogen content in the plasma (in the range 2-20 %), and at different substrate temperatures (in the range 400-800 °C). The samples were used to conduct leakage current tests in PBS (phosphate buffered solution) to test the hermetic/bio-inert properties of UNCD coatings for protection of a Si-based microchip being developed as part of an artificial retina. The data revealed that UNCD grown using 2% hydrogen in the plasma and $\sim 400^\circ\text{C}$ substrate temperature exhibit the lowest leakage current ($\sim 4 \times 10^{-7}$ A/cm² at -5 V) when tested in the PBS solution. Possible mechanisms responsible for the effect of hydrogen incorporation in increasing the electrochemical inertness of UNCD coatings will be discussed. In addition, in vivo tests of bioinertness of UNCD coatings were conducted via implantation of UNCD-coated Si samples into rabbit eyes. All in vivo and in vitro test results showed that UNCD coatings have good biocompatibility and biostability with the physiological environment. These studies demonstrate that UNCD is a promising candidate as hermetic/electrochemically inert coating for bioimplantable devices. This work was supported by the DOE-Office of Science-Materials Science under Contract No. W-31-109-ENG-38.

10:45 AM T4.7

Surface Functionalisation of Spherical Diamond Particles. Phillip John¹, Michael W. Anderson¹, Fraser A. Gray¹, Jae-Kap Lee^{1,2} and Jin-Yul Lee²; ¹School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, United Kingdom; ²Thin Film Material Research Center, Korea Institute of Science and Technology, Seoul, South Korea.

Homogeneous nucleation within a multi-cathode dc arc [1] results in the formation of spherical polycrystalline diamond particulates rather than conventional thin films. By controlling the arc conditions the particles can be synthesised with diameters lying in the range between 100 and 600 nm. Larger spherical particulates have been grown by depositing diamond on silica spheres in the 5-50 micron range. The advantage of the latter technique is that hollow shells of diamond can be fabricated by chemically etching the silica core. These new forms of diamond have many potentially important biosensor applications [2-3] due to their large surface area for conjugation to large biomolecules such as enzymes [2], DNA [3] and proteins [4]. The particles were thermally oxidised at temperatures $< 550^\circ\text{C}$ under one atmosphere pressure of pure, dry oxygen to create oxygen termination sites [5] which are predominantly carbonyl, $>\text{C}=\text{O}$, functional groups [6]. Subsequently the surfaces of the powders were functionalised under mild conditions with precursors, such as 4-(trifluoromethyl) benzylamine, containing the reactive amine, $-\text{NH}_2$, functional group in solution and characterised by FTIR and high resolution XPS analysis. Reduction of the labile imine groups produces a strongly covalent linkage to diamond surfaces for subsequent fabrication of biosensors. Further applications of the diamond micro- and nano-particles will be described. References. 1. JK Lee, Y-J Baik, KY Eun, J-Y Lee, J-W Park and P John, *Synthesis of Diamond Spheres, Advanced Materials/CVD*, 10 (92004) 133. 2. CE Troupe, IC Drummond, C Graham, J Grice, P John, JIB Wilson, MG Jubber and NA Morrison, *Diamond Based Glucose Sensors, Diamond and Related Mater.*, 7 (1998) 575. 3. WS Yang, O Auciello, JE Butler, W Cai, JA Carlisle, J Gerbi, DM Gruen, T Knickerbocker, TL Lasseter, JN Russell Jr., LM Smith and RJ Hamers, *Nature Materials*, 1 (2002) 253. 4. A Hartl, E Schmich, J A Garrido, J Hernando, S C R Catharino, S Walter, P Feulner, A Kromka, D Steinmuller and M Stutzmann, *Protein-modified Nanocrystalline Diamond Thin Films for Biosensor Applications, Nature Materials*, 3 (2004) 736. 5. P John, N Polwart, CE Troupe and JIB Wilson, *The Oxidation of (100) Textured Diamond, Diamond and Related Mater.*, 11 (2002) 861. 6. P John, N Polwart, CE Troupe and JIB Wilson, *The Oxidation of (100) Diamond, J. Amer. Chem. Soc.*, 125 (2003) 6600.

11:00 AM T4.8

Biofunctionalization of Oxidized Nanocrystalline Diamond Surfaces. Jorge Hernando, Jose A. Garrido and Martin Stutzmann; Walter Schottky Institut, Technische Universitaet Muenchen,

The achievement of conducting nanocrystalline diamond (NCD) at a relatively low cost with nearly the same exceptional properties as single crystal diamond and the subsequent immobilization of organic molecules on conducting NCD thin films [1,2] are attracting a lot of interest in the field of diamond-based biosensors. The functionalization approach of references 1 and 2 starts with a long photochemical process to bind an amine-terminated hydrocarbon chain on a Hydrogen-terminated surface. The progress in this promising field requires new immobilization alternatives in order to be compared with the photochemical process. Here we propose the use of oxidized NCD surfaces as the starting point of the functionalization, what implies new immobilization chemistries, at least for the coupling molecule between the surface and the biomolecules. Besides, due to the fabrication of oxidized structures on the nanometer scale with the help of local anodic oxidation assisted by atomic force microscopy [3], the functionalization of the oxidized surfaces could take advantage of the design of sensors on the nanoscale, which are characterized by a higher sensitivity and the achievement of denser arrays than conventional micro-sized sensor devices. Different oxygen-related groups, such as hydroxyl, carbonyl and/or ether groups, may be present at the NCD surface after oxygen plasma-induced oxidation. Therefore, a different coupling molecule can be chosen for each of these surface groups. For comparison, the functionalization of (100) and (111) single crystal diamonds is also studied. X-ray photoelectron spectroscopy (XPS), contact angle measurements, fluorescence microscopy, atomic and Kelvin force microscopy are used to characterize the attachment of the coupling molecules. After this initial treatment, the surface is ready for further processes to bind biomolecules, such as proteins, which are analyzed by electrochemical measurements after their attachment to an NCD electrode. First experiments use the 3-aminopropyl-triethoxysilane (APTES) molecule, expecting hydroxyl groups on the NCD surface. The attachment is confirmed by XPS measurements, and the later binding of horseradish peroxidase (HRP) proteins to an APTES-modified NCD electrode is studied by electrochemical measurements. [1] W. Yang, O. Auciello, J. E. Butler, W. Cai, J. A. Carlisle, J. E. Gerbi, D. M. Gruen, T. Knickerbocker, T. L. Lasseter, J. N. Russell, L. M. Smith and R. J. Hamers, *Nature Materials* 1, 253 (2002). [2] A. Haertl, E. Schmich, A. A. Garrido, J. Hernando, S. C. R. Catharino, S. Walter, P. Feulner, A. Kromka, D. Steinmueller and M. Stutzmann, *Nature Materials* 3, 736 (2004). [3] K. Sugata, M. Tachiki, T. Fukuda, H. Seo and H. Kawarada, *Jpn. J. Appl. Phys.* 41, 4983 (2002).

11:15 AM *T4.9

Diamond Thin Films: Interfacing Microelectronics to Biological Systems. Robert J. Hamers, Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin.

Recent studies have demonstrated that diamond thin films provide an extraordinarily stable platform for linking microelectronics with biological systems. The covalent modification of diamond surfaces with biomolecular recognition elements such as DNA or antibodies provides biological specificity. Biological binding events can be directly converted into electrical signals by taking advantage of the molecular field effect, in which binding of a target biomolecule to the surface induces a change in the space-charge region of the diamond thin film. The electrical response of the space-charge region can be measured either perpendicular or parallel to the interface. In the perpendicular arrangement, impedance spectroscopy can be used to detect DNA hybridization and antibody-antigen binding in real time. In the parallel arrangement, use of two electrodes on the surface leads to the fabrication of a biologically-sensitive field effect transistor ("Bio-FET") in which the nascent charge on the molecule directly induces a molecular field effect. We demonstrate the fabrication and characterization of a direct Bio-FET. The use of the native charge of the biomolecules instead of relying on more complex schemes such as enzyme reactions, pH changes, or redox reactions is significant because it provides a pathway for parallel electronic detection in electronic bio-arrays without interference between adjacent biomolecular recognition sites. To fabricate very small, ultra-dense bioarrays, it is necessary to develop new way of functionalizing surfaces with specific biomolecular recognition events. In addition to using electrical signals to probe biological binding events, it is possible to use electrical signals to *control* the biomolecular functionalization of nanocrystalline diamond and related carbon-based materials such as carbon nanotubes and carbon nanofibers. This ability is based upon the electrically-driven reduction of a surface nitro-group to an amino-group, which can then serve as the basis for functionalization of array elements. We demonstrate the fabrication of small biomolecular arrays on diamond-coated surfaces as well as surfaces modified with carbon nanotubes and carbon nanofibers. Spatial resolution in the submicron range can be achieved without the use of micro- or nano-fluidics. Ultimately, one can use electrical signals both to fabricate arrays and to characterize their electrical response as the basis for biomolecular sensing.

SESSION T5: Integration of Carbon and Dissimilar Materials and Diamond and DLC Devices
Chairs: Gerardo Morell and Ralf Spitzl
Friday Afternoon, April 1, 2005
Room 2012 (Moscone West)

1:30 PM *T5.1

Diamond as a Material for High Performance Micro and Nano-Scale Resonators. Brian H. Houston, National Research Laboratory, Washington, D.C., District of Columbia.

Microscale resonators provide the promise of new solutions to traditional problems in a number of areas. However, the scaling of the associated mechanical loss is not presently understood. Towards this end, we discuss several loss mechanisms that include thermoelastic (TE) dissipation due to transverse thermal currents and losses related to plasma induce damage, attachment loss, metallic films, and fluid loading. Temperature dependent losses will also be discussed that reveal a previously unknown dissipation mechanism due to small amounts of water adsorbed onto the surface of a high performance silicon microscale resonator. The Q factor was measured from 25K - 300K for in 1.5 μm thick single-crystal silicon resonator. Room temperature Q factors > 650,000 were observed and Q's as high as 1.3×10^6 we observed at Helium temperatures. Performance is fundamentally limited by TE loss and is achieved after the repair of plasma-induced damage and the influence of adsorbates. Our results agree well with Zener's model with modification to include a flexural energy participation factor. TE damping can be significant for silicon based oscillators and persist down to 50 nm scale structures and even for nominally torsional modes, which one might conclude, have no loss. Given the importance of this mechanism, in silicon structures, we will discuss the role of material properties associated with this and explore the potential of devices fabricated from nanodiamond films grown by microwave enhanced chemical vapor deposition (CVD). In addition to a higher sound speed, diamond should have lower TE related losses due to a lower thermal expansivity and a higher diffusivity of diamond relative to silicon. However, the internal friction of nanodiamond materials has not been reported to date. We will discuss recent thickness and temperature dependent measurements of the internal friction of nanodiamond films fabricated at the Naval Research Laboratory by CVD and use these results to anticipate the ultimate performance of micro and nano-scale resonators vice silicon. [Work supported by ONR and DARPA].

2:00 PM T5.2

Immobilization of Redox Enzyme on Functionalized Ultrananocrystalline Diamond Surfaces. Jian Wang, Nevin Naguib, Orlando Auciello and John A. Carlisle; Materials Science Division, Argonne National Lab, Argonne, Illinois.

The coupling of biological molecules with inorganic materials to form well-defined and robust hybrid bio-inorganic interfaces has attracted considerable attention because of their potential importance in fields such as molecular electronics, biomedical implants, and biosensors. Ultrananocrystalline diamond (UNCD) possesses a unique combination of chemical, mechanical, thermal, and electrical properties, which makes it a promising platform material for biointerfaces. Consequently, we have developed different surface functionalization strategies to covalently immobilize organic layers and eventually redox enzymes onto UNCD surfaces. Manipulating the chemistry of the tethered organic overlayer allows for the control over the UNCD surface hydrophobicity and charges. Electrochemical techniques, i.e., cyclic voltammetry and ac impedance measurements are used to perform the surface functionalization as well as to study the charge transfer mechanism. The success and the stability of the redox enzyme on the modified UNCD surface has been characterized by spectroscopy (FTIR, fluorescence), atomic force microscopy and biochemical assays. Sensing applications based on the integration of functionalized UNCD thin films with electrochemical detection techniques will be also described.

2:15 PM T5.3

Diamond FETs Biosensor for Detect the Label-Free DNA by its Intrinsic Molecular Charge. Kwangsup Song^{1,2}, Zhang Guojun^{1,2}, Yusuke Nakamura^{1,2}, Junghoon Yang^{1,2}, Hitoshi Umezawa^{1,2}, Ohdomari Iwao^{1,2} and Hiroshi Kawarada^{1,2}; ¹Science and Engineering, Waseda University, Tokyo, Japan; ²Nanotechnology Research Center, Waseda University, Tokyo, Japan.

In the methods used normally, to readout the biological signal requires the attachment of reporter molecules such as fluorescent, redox, or radioactive labels. Although label-dependent methods achieve the high sensitivity, eliminating the labeling steps has the advantage of simplifying the readout process, low coast, miniaturization, increasing

the speed and ease of nucleic acid assays. Here we introduce the diamond electrolyte solution-gate-field-effect transistors (SGFETs) for the highly sensitive and label-free detection of DNA hybridization. Real-time and static characteristics of FETs based sensors for DNA has been demonstrated. Diamond meets the requirements of robust biosensing devices because of its wide potential window, chemical-physical stability and biocompatibility. Sub-nanomolar (100 pM) complementary DNA concentrations can be detected within seconds, non-complementary and a single base mismatch within 21-mer oligonucleotides can be detected clearly. The sensors were fabricated diamond SGFETs show promise for future electronic DNA arrays, real-time, label-free detection and rapid characterization of nucleic acid samples in pharmacy and in vivo diagnostics of disease.

2:30 PM T5.4

A Novel Approach for Integrating Tetrahedral Amorphous Carbon Films with Nanoengineered Surfaces and Nanoparticles. Mevlut Bulut and Renato P. Camata; Dept. of Physics, Univ. of Alabama - Birmingham, Birmingham, Alabama.

The integration of tetrahedral amorphous carbon (ta-C) with nanostructured surfaces and nanoscale objects of different materials has long been recognized as a potential pathway for important applications ranging from high-density magnetic storage to biological sensing. Such integration has often proven to be a challenging materials fabrication problem. Most studies to date have shown, for example, that nanoparticle incorporation is often deleterious to some of the most important properties of ta-C such as its low coefficient of friction and wear rate. This property degradation is due in part to the disruption of the conditions for ta-C deposition and the inability to control the multiple internal interfaces that constitute ta-C composites. In this study we explore the use of a novel technique known as Nanoparticle Beam Pulsed Laser Deposition (NBPLD) that allows a new level of control in the integration of ta-C films with nanoparticles and nanoengineered surfaces. In this approach laser-generated nanoparticles in the 3-20 nm size range are entrained in a carrier gas, size classified and delivered to a substrate as a nanoparticle beam. This method has the potential to generate a focused nanoparticle beam through aerodynamic focusing enabling the deposition of nanoparticles with a spatial resolution within tens of microns. This nanoparticle source has been integrated into a conventional PLD system configured for the production of a gas-phase dominated plume appropriate for ta-C deposition. Nanoparticles of well-controlled size, structure and chemical composition are thus deposited using NBPLD while ta-C is sequentially deposited by conventional PLD. This combination of techniques allows ta-C integration with nanoparticle-modified surfaces that may act as seeds for controlling film growth; as discrete nanoparticle layers that may become embedded within the ta-C film itself; and as top layers that may assist in ta-C surface functionalization. The advantages of this approach rest on its applicability to a variety of nanoparticle materials whose suitability for integration with ta-C may be evaluated quickly and on its ability to manipulate the nanoparticle diameter and concentration, independently of the conditions required for successful ta-C deposition. Our goal is to use these various modes of size-selected nanoparticle integration to modulate the ta-C growth dynamics, its mechanical and tribological properties, and explore an alternative route for relief of residual stress. A model system for our experiments involves the controlled incorporation of titanium, nickel, and cobalt nanoparticles in micron thick ta-C layers deposited on mirror polished Ti6Al4V alloy substrates. Metal nanoparticles are deposited by ablating the corresponding metallic targets at 100 Torr in the NBPLD source using a KrF excimer laser (248 nm) at fluences of 1-5 J/cm² while deposition of ta-C is achieved by ablation of pyrolytic graphite targets in high vacuum at 5-15 J/cm².

2:45 PM T5.5

Nanocrystalline Diamond-based Nanomechanical Resonators Incorporating PZT for Coupling of Electrical and Mechanical Signals. K. Son¹, R. Toda¹, T. George¹, R. W. Fathauer², L. Wang², S. M. Phillips², B. Lambert³, D. P. Weitekamp³, B. H. Houston⁴, J. F. Vignola⁴, J. E. Butler⁴, W. Fan⁵ and O. Auciello⁵; ¹Jet Propulsion Lab., Pasadena, California; ²Arizona State University, Tempe, Arizona; ³California Institute of Technology, Pasadena, California; ⁴Naval Research Laboratory, Washington, District of Columbia; ⁵Argonne National Laboratory, Argonne, Illinois.

High-frequency mechanical resonators with high quality factor Q are of interest for a variety of applications, including RF communications. For a given geometry, resonance frequencies are determined by the mechanical properties of the resonator. In particular, the square root of the ratio of the Young's modulus (for flexural modes) or shear modulus (for torsional modes) to the density. In addition to being an excellent material by this measure, the outstanding thermal properties of diamond makes it a particularly attractive material as regards phonon loss mechanisms that can limit Q. Finally, the low surface reactivity of diamond reduces the potential for losses due to surface

effects, an increasing concern as dimensions are reduced in order to increase frequencies. To this end, we are developing diamond-based, nanometer-scale ferroelectric mechanical resonators. Nanomechanical resonators offer small volumes, high resonance frequencies, and high sensitivities. We are focusing our efforts on torsional motion in order to take advantage of our novel signal transduction method, in which a voltage exerts a torque on a block of lead zirconate titanate (PZT). In our approach, nanocrystalline diamond torsional resonators are fabricated between thick RF metal lines. An RF voltage across the metal lines couples to the permanent dipole moment of a PZT block (used here for its ferroelectric rather than piezoelectric property) that has been grown on the diamond by MOCVD. This provides a driving torque resulting in an angular amplitude for the torsional resonator motion that scales with the RF signal strength at the resonance frequency. This motion may be detected optically via light scattering from Au nano-particles fabricated on top of the ferroelectric block or electrically by the current induced in the metal lines by the motion of the ferroelectric moment. In our work, resonators are fabricated with CVD nanocrystalline diamond films grown on the silicon oxide wafers. Electron beam lithography followed by fluorine-based reactive ion etching (RIE) methods is used to form the resonators. Nanometer-sized PZT blocks are created on the resonators by depositing the PZT film over a nanopatterned sacrificial film. Characterization of resonators is carried out experimentally using scanning Laser Doppler Vibrometry (LDV), and compared to numerical simulations of resonator performance using finite element-based structural dynamics codes. Initial characterization of a double-paddle nanomechanical diamond resonator without a PZT block shows resonances in the 10 MHz range.

3:15 PM *T5.6

Enzyme-Modified Nanocrystalline Diamond Electrodes for Biosensor Applications. Jose Antonio Garrido¹, A. Hartl¹, J. Hernando¹, M. Stutzmann¹, S. Walter², J. R. Retama³ and F. Lopez-Cabarcos³; ¹Walter Schottky Institut, Technische Universitaet Muenchen, Munich, Germany; ²Institute for Organic Chemistry and Biochemistry, Technische Universitaet Muenchen, Munich, Germany; ³Departamento Fisico Quimica Farmaceutica, Facultad de Farmacia, UCM, Madrid, Spain.

Diamond exhibits several special properties, e.g. a good biocompatibility, low background current, and a large electrochemical potential window, which make it particularly suitable for biofunctionalization and biosensing. In this contribution, we show that enzymes can be attached covalently to nanocrystalline diamond thin films. Moreover, we have confirmed that, although immobilized at the surface, the biomolecules are still fully functional and active. Different routes are available for the functionalization of nanocrystalline diamond surfaces depending on the surface termination, hydrogen or oxygen. Hydrogen-terminated nanocrystalline diamond films can be modified using a photochemical process to generate a surface layer of amine groups, to which proteins can be covalently bound in several following steps. For comparison, oxygen-terminated NCD films have been functionalized using different chemical methods. The enzymes catalase and horse-radish peroxidase were immobilized on the modified NCD electrodes, and the successful attachment was confirmed by measuring the enzyme activity. Impedimetric experiments were also used to study the surface modification. The enzyme-modified diamond electrodes exhibit direct electrochemical charge transfer between the enzyme redox center and the electrode. The enzyme-NCD electrodes were also used as H₂O₂ sensors. In the presence of H₂O₂, a large cathodic current is observed due to the reduction of H₂O₂ catalyzed by the enzyme modified electrode. Catalase-modified NCD electrodes stored at 4°C in buffer solution were tested eight weeks after fabrication. Cyclic voltammetry experiments confirmed that the enzymes were still active and showed the same characteristic redox peaks related to the direct electrochemical charge transfer.

3:45 PM T5.7

Diamond-like Carbon Devices: Influence of Nanoclustering. David Carey and Ravi Silva; University of Surrey, Guildford, United Kingdom.

Despite the ready ease of low temperature large area deposition, practical electronic devices based on diamond-like carbon (DLC) have largely failed to be produced. DLC films can be considered as a mixed phase material with the electronic properties being controlled by the nanometer sized sp² phase and the mechanical properties being controlled by the sp³ phase. We show that the disorder plays an important role in the sp² phase which in turn affects the electrical conduction through the film. We further show that localised energy deposition through careful choice of ion energy and dose, how low mass ion implantation leads to improvements in the electrical conductivity and that this improvement is related to controllable changes in the sp² phase. This gives rise to nanometer sized dielectric inhomogeneities which are also shown to play a role in controlling the field induced electron emission characteristics from these films.

Extensions of this model to other material systems such as nitrogenated ultrananocrystalline diamond are also presented.

4:00 PM *T5.8

Sulfur-Assisted Chemical Vapor Deposition of Nanocrystalline Diamond: Properties and Applications.

Gerardo Morel^{1,5}, S. Gupta², B. R. Weiner³, B. L. Weiss⁴, F. Piazza⁵, J. De Jesus⁵, A. Gonzalez-Berrios⁵, R. Velazquez⁵, E. Mujica⁵, V. Makarov³ and M. Buzaiianu⁵; ¹Dept of Physical Sciences, University of Puerto Rico, San Juan, Puerto Rico; ²Department of Physics, Missouri State University, Springfield, Missouri; ³Department of Chemistry, University of Puerto Rico, San Juan, Puerto Rico; ⁴Department of Physics, Pennsylvania State University at Altoona, Altoona, Pennsylvania; ⁵Department of Physics, University of Puerto Rico, San Juan, Puerto Rico.

The addition of trace amounts of sulfur, in the form of hydrogen sulfide (H₂S), to the diamond chemical vapor deposition (CVD) reaction produces profound changes in the gas phase chemistry. Thermodynamic equilibrium calculations have shown that at temperatures above 2000°C, H₂S is converted into CS. This is what is expected to happen near the filament, which is at 2500°C. At temperatures below 1000°C, which is the temperature range of the substrate, H₂S is more stable. We can expect that during the hot filament CVD process CS is formed near the filament and diffuses to the growing film surface where it is adsorbed. At the surface, CS reacts to H₂S and leaves the carbon for diamond growth. CS thus enhances the carbon transport to the growing film surface, inducing continuous secondary nucleation that leads to the formation of nanocrystalline diamond. The corresponding films' field emission, radiation endurance and thermoelectric properties are also affected by the introduction of sulfur, and can be enhanced by proper choice of deposition parameters. Our experiments have shown a four-fold increase in the deposition rate, from 0.1 to 0.4 μm with 500 ppm of hydrogen sulfide, for films grown at 700°C, which is the typical substrate temperature. Further, for films grown under 0.3% CH₄ and 500 ppm H₂S, the Raman intensity increases by an order of magnitude as the substrate temperature is reduced from 900 to 400°C. Moreover, when 2.0% CH₄ is employed without H₂S, only nanocomposite carbon is grown, but the addition of 500 ppm H₂S and the reduction of the substrate temperature results in microcrystalline diamond films. These results clearly indicate that further reduction in the substrate temperature is possible while keeping high-quality diamond films, enabling the deposition of diamond films on temperature-sensitive substrates. The changes induced in the gas phase composition by the addition of H₂S during HFCVD were studied by Cavity Ring Down Spectroscopy (CRDS). We performed experiments designed to detect the HS radical concentration as a function of distance from the reactor filament. The experimental setup used for such measurements is optimized for observation of the $0(X^2\Pi_{1/2,3/2}) \leftarrow 1(A^2\Sigma^+; \nu = 28010.72 \text{ cm}^{-1})$ transition of HS. Since the HS radical has high rotation constants both in ground and excited states ($B_X = 9.461$ and $B_A = 8.521 \text{ cm}^{-1}$), the rotation spectrum of this radical is resolved even at high temperatures and in relatively dense conditions.

4:30 PM *T5.9

Microwave assisted Plasma Systems and Processes for Large Area Diamond Film Growth. Ralf Spitzl and Hildegard Sung-Spitzl; iplas GmbH, Troisdorf, Germany.

Microwave assisted CVD is a widely used method for diamond deposition. Especially for coating of high quality diamond, single crystal homo- and hetero epitaxy as well as the new Ultra Nano Crystalline Diamond (UNCD) from Ar/CH₄ gas mixtures microwave powered reactors are used. The advantages of microwave plasmas are very good stability of plasma, clean plasma conditions and nearly no limits in terms of gas mixture. It can be used in a wide pressure range from ~ 0,1mbar up to several 100 mbar. No filament or electrode material is present in the discharge. The growth rate strongly depends on the plasma conditions (e.g. pressure, gas mixture) and is found in the range between 0,1 μm/h up to several 10μm/h. The homoeptaxial growth on diamond substrates show a increase of growth rate up to a factor of ~3 compared to non diamond substrates like silicon. The scale up of diamond processes is an important issue for commercialising the technology. For hot filament systems large area systems are available up to e.g. 500 mm x 1000 mm, but typical deposition rates are in the range of 0,1-1 μm/h. Such systems are widely used for tool coating or coating of electrodes, where contaminants and crystallinity are acceptable. With introduction of modern microwave plasma systems like the CYRANNUS (Cylindrical Resonator with Annular Slots) systems the coating area could be increased significantly. This is achieved by integrating the electromagnetic fields of a homogenously fed multi antenna structure into the formation of microwave plasma. Additional advantage of such coupling structures is given by the possibility of top and bottom access to the plasma. At microwave frequency of 2,45 GHz a coating over 200mm Si wafers could be achieved with a CYRANNUS I - 10,5".

The frequency scale of CYRANNUS I - 6" (2,45 GHz) yield a CYRANNUS I - 16" (915 MHz) plasma source. First diamond coating experiments with hydrogen/methane mixtures yield a coating over 200 mm Si wafers with no fringes visible. It is expected that coatings over 300mm wafers are feasible by further process optimization.