Synthesis and Processing of Carbon-Based Nanostructured Materials

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Motivation

Carbon-based materials exhibit unique physical, chemical, mechanical, tribological, and transport properties that are driven by the many different bonding configurations available to carbon. For example, diamond exhibits extreme properties of hardness, atomic density, thermal conductivity, and optical transparency ranging from the far infrared to the near UV. Nanocrystalline diamond films exhibit unique electronic, mechanical, tribological and optical properties induced by the extreme small size of the grains (2-5 nm) and the grain boundaries (0.3-0.4 nm). Diamond-like carbon is an amorphous mixture of 4- and 3-fold bonded carbon with properties that can be tailored between graphite and diamond. Fullerene molecules have a unique structure, while carbon nanotubes may be the strongest material in the world and exhibit significant variations in electronic properties for single-walled tubes. Controlled passivation of dangling σ-bonds of surface carbon atoms by hydrogen in diamond and diamond-like carbon films results in super-low friction and wear in sliding bearing applications. Moreover, the surfaces of all of these structures exhibit unusual chemical properties, from the negative electron affinity of hydrogen-terminated diamond to the chemical stability of diamond, fullerenes and nanotubes. This morphological flexibility makes carbon-based materials inherently multifunctional. In addition, these materials are compatible with both inorganic and biological systems, making devices based on carbon materials especially attractive.

Recent advances in micro and nanofabrication techniques have made possible the development of microscale and perhaps even nanoscale devices that capitalize on the many intrinsic strengths of carbon-based materials. Thus, while silicon has been the basis of modern electronics and the digital revolution, we envision future multi-functional carbon materials systems that will enable a second revolution based on microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS). We hope to drive these materials into a regime where they can naturally interface both with electronic and biological systems. The focus of the proposed Project is to explore the fundamental science related to nanostructured carbon-based materials and devices.

Objectives

The objective of the proposed CSP Project is to advance the science and technology of carbon-based materials that will lead to the development of a new generation of MEMS and NEMS devices. The Project's activities will be focused on: a) investigation of fundamental processes and phenomena related to carbon materials in the various forms of micro- and nanocrystalline diamond, diamond-like carbon, nanofibers and nanotubes, and b) development of MEMS and NEMS devices and their implementation to enable the exploration of fundamental processes in carbon materials at the micro- and nanoscales. The Project will thus focus not only on nanoscience but also on the development of the microscale and nanoscale instrumentation needed to conduct that science. The overall approach of the Project is to effectively couple existing programs in carbon-based systems in order to enable collaborative interactions that would otherwise not occur. In addition, the proposed Project's research focus is directly related to a major area of new emphasis in DOE-BES, i.e., the National Nanotechnology Initiative, and also fits with DOE's programmatic objectives of supporting major centers of nanoscience research at several national laboratories.

PROPOSED RESEARCH PROGRAM

TASK 1: Synthesis, Processing, and Fundamental Mechanical and Tribological Properties of Carbon-Based Materials

Task Description

When mechanical structures shrink to the scale of microns and below, the forces that dominate surface interactions change. Available actuation forces and inertia become small compared to electrostatic, van der Waals, and meniscus interfacial forces. Thin film lithographic fabrication methods also result in structures that are compliant out-of-plane so that residual stresses or stress gradients can easily distort structures, rendering them useless. Understanding, measuring and ultimately controlling properties at this scale is therefore critical. Measuring the mechanical and tribological properties at the nanometer scale presents unique challenges that require novel instrumentation and/or the use of novel MEMS architectures. The proposed Project has unique personnel and infrastructure to perform such measurements and develop the required understanding.

The carbon materials chosen for investigation in Task 1 include amorphous diamond (a-D) carbon films produced at SNL via pulsed laser deposition [1] and ultrananocrystalline diamond (UNCD) films synthesized at ANL, using MPCVD [2]. SNL has extensive facilities for silicon and carbon-based MEMS manufacture, testing, and characterization. Examples include a polycrystalline silicon MEMS foundry with the world's most sophisticated process (SUMMIT) for design and fabrication of MEMS devices with up to five structural layers. Characterization facilities include automated wafer-level mapping of adhesion, elastic modulus, residual stress and stress gradients, as well as MEMS-based friction, wear, elastic modulus, and fracture strength determination. LBNL has developed a unique in-situ TEM nanoindentation system to study crack formation and defect propagation. We plan to leverage existing capabilities and develop new expertise throughout the program.

Preliminary experiments to investigate crack propagation indicate that forces that easily produce defects in silicon result in no visible effects in UNCD films. Pure tensile testing of 2×2 μm ligaments at SNL has provided invaluable statistical measurements of the fracture strength and modulus of silicon and amorphous diamond MEMS, and efforts are under way to duplicate these measurements on ANL's UNCD. The mechanisms of fracture and dependence on microstructure are not well understood for these materials. Diamond exhibits low friction coefficient and low wear rate in chemically passivating environments. Furthermore, the role of adsorption and desorption of environmental species on tribological processes is not known, so a key component of the proposed work will be TEM studies to relate the mechanical and tribological properties with film morphology.

The superlow friction and wear mechanisms of diamond and diamond-like carbon films are not yet fully understood, but it is believed that such low friction and wear values are associated with hydrogen on the sliding surface and within the films. Understanding of the fundamental tribological mechanisms of energy dissipation and wear of these films will be extremely valuable for the design and development of new carbon-based micromachines and related applications. Experimental work performed to understand the effect of hydrogen and other species on surface related tribological processes will include *in situ* studies, using time-of-flight ion scattering and recoil spectroscopy (TOF-ISARS)/(x-ray photoelectron spectroscopy (XPS) techniques available in a single system at ANL. This system is capable of providing unique atomic-scale insights into surface processes such as those related to critical tribological phenomena. Computational chemistry and molecular dynamics simulation methods will be used to provide information on interatomic bonding and surface structure in the low friction carbon films, to provide the fundamental information needed to understand the friction and wear mechanisms of these materials.

This task will focus on developing an understanding of microstructure effects on the strength and fracture properties of amorphous and nanocrystalline diamond, and on the role of adsorption, desorption, and surface chemical reactions on friction and wear of these materials. In situ TEM nanoindentation and microfabricated structures will be used to investigate strength, deformation and fracture phenomena. Self-mated sliding of blanket films in ultrahigh vacuum, oxygen and water vapor will be used to understand changes in tribological interactions due to adsorption and chemical reactions. Similar investigations will be carried out using microfabricated diamond friction structures to understand these effects at high shear rates. This understanding will enable the exploitation of the desirable mechanical and tribological properties, and chemical stability of diamond for MEMS devices. The work performed by the SNL and ANL groups indicate that it may be possible to integrate low stress, high strength diamond structures with an ultralow friction surface layer and dramatically increase the performance and reliability of a new class of microsystems based on carbon.

Team and Efforts

- T. Friedmann (SNL) will develop stress-free a-D MEMS and NEMS for fundamental studies of surface forces, tribology, fracture, and surface chemistry.
- T. Buchheit and M. Dugger (SNL) will use micromechanical test structures to relate strength and fracture to the nanostructure of diamond films, and to understand changes in friction and wear of these materials at high shear rates due to adsorption and surface chemical reactions.
- M. de Boer (SNL) will perform surface adhesion measurements on carbon-based MEMS structures.
- O. Auciello, J.A. Carlisle, and D.M. Gruen (ANL) will develop low stress, low wear and friction UNCD MEMS structures for studies of mechanical and tribological processes at the micro- and nanoscale
- L.A. Curtiss, P. Zapol, and S.R. Phillpot (ANL) will perform computer simulations to provide theoretical insight into the tribological properties and mechanical processes of carbon-based materials.
- A. Erdemir (ANL) will develop ultralow friction carbon films to tailor the frictional properties of UNCD, a-D and silicon surfaces, and perform experiments to understand the role of adsorption on the frictional behavior of these films.
- E. Stach (LBNL) will perform in situ TEM nanoindentation to investigate fundamental defect propagation in diamond materials.

Existing Projects:

Research on carbon films synthesized by pulsed laser deposition at SNL has resulted in amorphous diamond (a-D) which is extremely hard, wear-resistant, transparent, with optically smooth surfaces, and chemically inert. Unique features of this material include: the ability to tailor film stress from compressive through zero to slightly tensile; hardness and stiffness 90% that of diamond; very high wear resistance; surfaces that are intrinsically hydrophobic; extreme chemical inertness; biocompatibility; chemical compatibility with silicon processing; room temperature deposition; and the ability to control the film conductivity from insulating to conducting. Simple proof-of-principle micro-mechanical devices based on stress-free a-D have already successfully demonstrated [3]. Fig. 1 shows the working end of a MEMS tribology tester successfully fabricated in diamond.

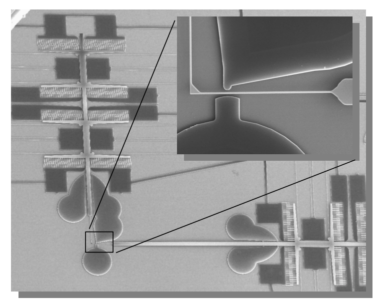

Fig. 1. Amorphous diamond friction tester (1mm×1mm).

Current micromechanical evaluations at SNL employ a “pull-tab” specimen, where a nanomechanical force-displacement probe (such as a nanoindenter) engages a micro-sized test structure. A typical test structure for a-D is illustrated in Fig. 2. Studies have been conducted on polysilicon samples and amorphous diamond (a-D) produced at SNL, which provided invaluable statistical measurements of the fracture strength, modulus, and fracture toughness of both materials. Further material response insight has been gained by combining microstructural analyses such as Transmission Electron Microscopy (TEM) and Electron Backscatter Diffraction imaging (EBSD). For example, lower strength measurements on tungsten-coated polysilicon samples were found to be caused by small precipitates which acted as crack nucleation sites near the tungsten-polysilicon interface. More complex micromechanical test specimens that use the same basic methodology are currently being fabricated, which are intended to provide more accurate fracture toughness and fatigue measurements of microsystem materials.

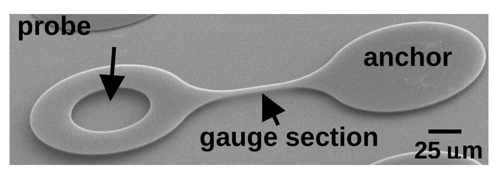

Fig. 2. Amorphous diamond tensile specimen.

Extensive measurements of adhesion in silicon MEMS have been made (SNL) using an automated probe station combined with an interferometric microscope to measure out-of-plane device deflections. These measurements have been invaluable in understanding and modeling adhesive forces on the microscale and similar studies will be performed in carbon based MEMS

Advancement of specimen designs and test procedures, enabled by glue funding, will permit a focus on nanostructured materials mechanical evaluation techniques. We believe that these techniques will have broad applicability beyond the proposed carbon based MEMS.

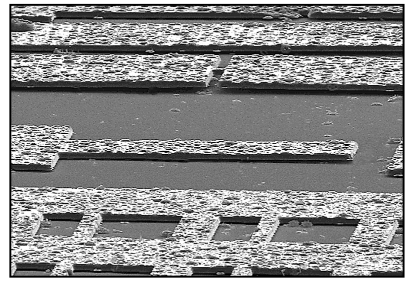

Fig. 3. UNCD-based MEMS cantileaver showing evidence of as-deposited low-stress (130μm×100μm).

Systematic research on carbon-based materials and coatings at ANL has led to the development of a new carbon film material with ultralow friction (NFC-nearly frictionless carbon), on the order of 0.005, in self-mated contacts in inert or vacuum environments. This level of friction is more typical of hydrodynamically lubricated systems and is unprecedented for solid-solid contacts. The film also provides extremely low wear rates (10^{-10} to $5x10^{-11}$ $mm^3/N \cdot m$) when sliding against coated steel or ceramic counterfaces. A combination of extreme wear resistance and very low friction makes these carbon films unique and potentially useful for microsystem applications. UNCD has been developed at ANL utilizing a gas phase carbon dimer growth species in microwave plasmas with little or no added hydrogen. Consequently, the activation energy is much lower than that for growth of diamond by other plasma-assisted processes, and UNCD can be grown at temperatures as low as 350 ºC. Fig. 3 shows UNCD MEMS structures made at ANL that exhibit very little curling or warping when released from the substrate, which is a clear indication that these films have very low stress [4]. ANL has also developed a unique time-of-flight ion scattering and direct recoil spectroscopy (TOF-ISARS) system, which will be upgraded to include an in situ pin-on-disk microtribometer. The track produced by the pin will be analyzed using the TOF-ISARS method, capable of providing information on the surface modification induced by the pin, as well as gas-induced effects, at relatively high background pressures. TOF-ISARS consists of three surface analytical methods, namely: (a) Ion Scattering Spectroscopy (ISS) (b) Direct Recoil Spectroscopy (DRS), and (c) Mass Spectroscopy of Recoiled Ions (MSRI). It is a highly surface sensitive, non-destructive analytical tool with a depth resolution extending to the two top monolayers of solid surfaces, and will provide unique insights into tribological processes on diamond and other surfaces at the nanoscale.

LBNL has developed a unique tool for observing fundamental deformation and fracture processes in real time and at high spatial resolution. A piezoelectrically actuated diamond nanoindenter has been integrated into a TEM specimen goniometer to allow quantitative measurements of load-displacement behavior to be correlated directly with images of microstructural response. Qualitative experiments on ANL's NCD material have dramatically demonstrated the inherent fracture resistance of blanket diamond films. S&P funding will allow quantitative comparisons to be made between NCD materials as a function of doping concentrations and amorphous diamond films as well as determination of basic material properties.

TASK 2: Fundamental Transport Processes in Nnanoscale Carbon-Based Materials

Task Description

Unlike any other amorphous or crystalline material, nanostructured carbon materials display highly localized electrical transport and electron emission characteristics, and they can be operated at substantially above ambient temperature. For example, images of field emission of nanocrystalline diamond films and carbon nanotubes display emission sites of less than 10 nm (Fig. 5). Because of the extreme thermal conductivity of diamond and other carbon materials, these sites can sustain enormous current densities. The primary goal of this task is to develop new approaches for highly localized electron transport and electron emission structures that may be integrated into complex chemical and biocompatible microsystems. Possible examples include cold-cathode electron sources, chemical and biological sensors, and local x-ray or plasma sources. Nanostructured carbon materials are uniquely able to fulfill this vision, and the team for this proposal brings both the expertise and the capabilities to enable this vision. The challenges extend from understanding the fundamental physics of the transport and emission phenomena to the development of new approaches to accurately synthesize, selectively process and integrate these carbon materials into new micro and nanosystems.

Nitrogen-Doped UNCD Films

One of the most exciting advancements in nano-materials is the development of new phases of diamond-like thin films, including amorphous diamond discussed in the previous section and phase pure *ultrananocrystalline* diamond (UNCD) discussed below. For amorphous diamond significant sp^2-bonded carbon fractions govern the electrical and optical properties and the conduction mechanism can best be described as polymeric in nature with transport governed by electron-hopping between sp^2-carbon chains. UNCD is mostly sp^3 bonded, but significant sp^2 bonding can exist at defects, grain boundaries, and stacking faults. In general, control of the sp^3/sp^2 bonding in these materials is critical in determining their electrical properties. These materials have already demonstrated significant potential in MEMS applications, but the potential for integration of transport and emission structures will enable the advanced applications noted above. In this project we propose to initiate a comprehensive study (fundamentals, materials, processing, and theory) of doping of UNCD materials with engineered variation in the sp^3/sp^2 bonding. We expect that this study will lead to new approaches for transport devices that can be operated at and above ambient temperature.

Electron transport and field emission from nanostructured diamond thin films are two intimately related phenomena that appear to be largely controlled by grain boundary-dominated transport processes and/or field enhancement at localized sites. In fact, the fundamental processes are still the subject of substantial debate since traditional models cannot explain the highly localized character of the emission.

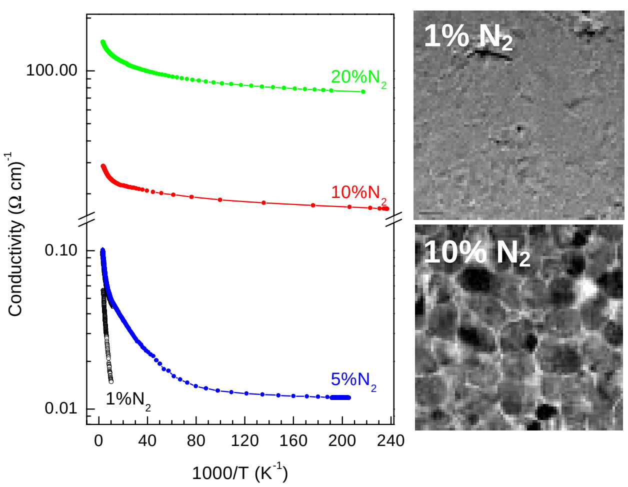

Fig. 4. (Left) Temperature dependent conductivity data taken from a series of nitrogen-doped UNCD thin films samples grown at ANL. (Right) TEM micrographs (100×100 nm) of UNCD thin films synthesized with either 1% or 10% nitrogen added to the plasma.

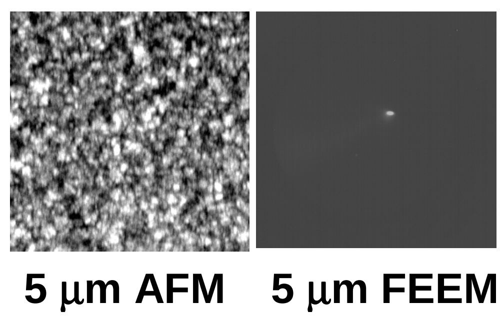

Fig. 5. Comparison of AFM and Field Electron Emission Microscopy (FEEM) images of a film with nanocrystalline diamond domains. The AFM displays a relatively smooth surface (RMS of 15 nm) with nm scale domains, and the FEEM displays highly localized, high intensity emission from a single site. Higher resolution FEEM images have indicated that the emission sites may be less than 10 nm in diameter

Over the past several years ANL has developed a microwave plasma chemical vapor deposition (MPCVD) technique to grow UNCD thin films [2]. This technique involves using either a C_{60}/Ar or CH_4 (1%)/Ar plasma that leads to the generation of C_2 molecular precursors, which in turn result in the growth of phase-pure films with 2-5 nm grain sizes and 0.3-0.4 nm wide grain boundaries [5]. UNCD films exhibit a number of interesting materials properties, including enhanced field emission [5, 6], electrochemical [7], as well as mechanical, tribological, and conformal coating properties suitable for microelectromechanical system (MEMS) devices [4].

Previous efforts to synthesize diamond or diamond-like carbon thin films with high n-type conductivity have been largely unsuccessful [8-11]. Over the past year ANL has focused on the incorporation of dopant gases into the normal Ar-CH_4 plasma used to deposit UNCD films In particular, the team has studied the addition of nitrogen, with the goal of achieving true n-type doping with high conductivities, carrier concentrations and mobilities. Films prepared without adding nitrogen are highly insulating, whereas the conductivity of the UNCD films increases from about 10^{-3} $(\Omega\cdot cm)^{-1}$ to 150 $(\Omega\cdot cm)^{-1}$ for films grown with 1% or 20% nitrogen in the plasma, respectively [12] (see Fig. 4). Preliminary field emission studies indicate that emission from flat nitrogen-doped films have low threshold voltages and stable emission currents. Density functional based molecular dynamics simulations indicate that nitrogen is likely to be in the grain boundaries and is responsible for new electronic levels in the diamond band gap.

The central question to be addressed is the mechanism for such high conductivities and field emission characteristics through a combination of transport measurements and quantum chemical calculations at ANL, PEEM and FEEM studies at NCSU (Fig. 5), and TEM-based electron holography studies at NW (Fig. 6).

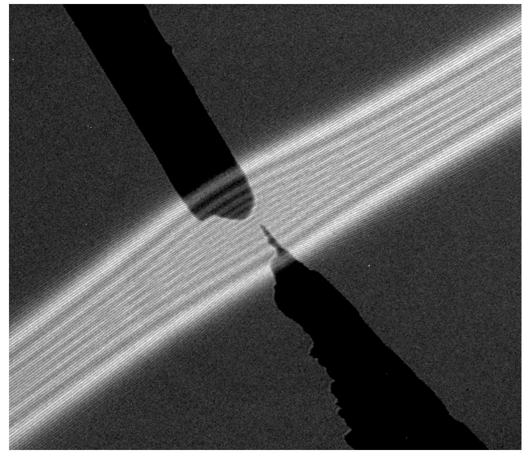

Fig. 6. Hologram of early stage of field emission from an individual, isolated carbon nanostructure from NW.

Integrated Carbon Materials

Although perfect single–walled carbon nanotubes (SWNTs) display unusual structural and electronic properties as a function of their diameter and helicity, as well as quite low threshold voltages (~1-3 V/μm) for field emission (FE) of electrons, the integration of *single* SWNTs into field-emitting or related devices is still problematic for several reasons. First, SWNT growth requires high temperatures (>900°C) that may be incompatible with a multistep device process involving either CMOS or MEMS processing. Second, isolated vertically aligned SWNTs, though strong, also will be flexible, so the emitting tip could easily move during FE, as has been observed during FE from random "forests" of SWNTs. Third, the catalytically controlled growth of isolated SWNTs will require very small (~1-2 nm diameter) metal catalyst particles (Ni, Fe, Co, etc) for which it is difficult to prevent a reaction with the substrate during heating to the growth temperature. Therefore, reliable growth of isolated, vertically aligned SWNTs is difficult and has not been demonstrated.

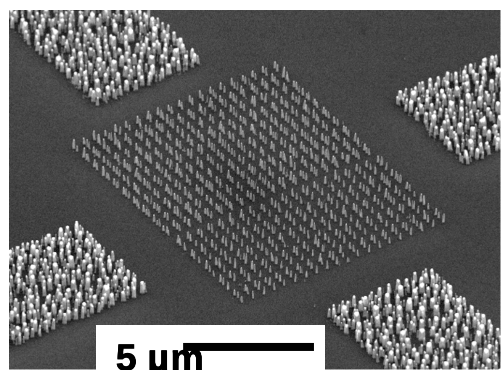

Fig. 7. vertically aligned carbon nanofibers (VACNFs) grown at ORNL.

In contrast, the ORNL team has recently developed a DC plasma enhanced CVD (PECVD) process for growth of isolated vertically aligned carbon nano*fibers* (VACNFs) with tip diameters of typically ~ 30 nm and heights of a few μm, depending on the duration of growth (Fig. 7) [13]. Growth of these VACNFs is highly deterministic, in that one VACNF will grow wherever an appropriate-sized catalyst particle is formed (using e-beam lithography for patterning), and complete arrays can be grown at moderate temperatures <600°C, as shown in the accompanying SEM images. However, the wall structure of VACNFs is imperfect, consisting of disordered layers of sp^2–bonded graphitic carbon. The field emission characteristics of these VACNFs also have been studied, and VACNFs with an aspect ratio AR ~ 100 (where AR = height / tip radius) are moderately good field emitters with a threshold field (for 1 nA current) of ~ 30 V/μm [14].

Concurrent with this work, ANL developed a MPCVD technique for depositing UNCD films. These films contain a significant fraction of sp^3–bonded carbon but with a high surface-to-volume ratio because of their nanoscale grain size, and probably numerous sp^2–bonded regions associated with the grain boundaries. These UNCD films are also good field emitters, due to either hydrogen passivation of the UNCD grains, resulting in a low electron affinity of these sp^3–bonded regions, or to quantum confinement effects at the grain boundaries and a corresponding raising of the electronic energy levels there, also resulting in a low effective electron affinity. However, it is currently not understood which grains or boundaries of the UNCD films are good emitters, or what is the macroscopic emission site density. This is information is necessary to control the emission site density in view of possible critical applications.

In this research, the ORNL and ANL processes will be combined to grow *a composite nanocarbon system* that incorporates the best features of both of the resulting materials. VACNFs will be grown by the ORNL PECVD process and a UNCD film then will be deposited over them using the ANL MPCVD process. For field emission there will be strong geometrical enhancement of the applied field at the VACNF tips, and this may be augmented by the low electron affinity of the UNCD coating. This combination could result in the synthesis of an array of field emitters with both a well-defined site density (the VACNF locations) and quite low emission threshold due to the additional geometrical enhancement of the already low UNCD emission threshold. Extensive studies on the synthesis and electron emission properties of these composite carbon structures will be performed using various analytical techniques such as I vs V electron emission measurements, photoelectron emission imaging of emission sites using a photoelectron emission microscope (PEEM), and in situ TEM characterization of electronic processes and correlation with nanocomposite microstructure using a unique TEM holography technique in conjunction with an integrated electric nanoprobe in a TEM available at Northwestern University.

The fundamental science to be performed in this task could lead to the development of ultra-small (mesoscale) field emission-based electron sources using nanocomposite carbon emitters. These sources could be integrated into MEMS and NEMS to produce high dynamic range sensors based on electron emission. The nanoscale electron beams produced by these sources could also be used for local light sources or for initiating local chemical reactions.

Team and Efforts

- J.A. Carlisle, O. Auciello, and D.M. Gruen (ANL) will synthesize nitrogen doped UNCD thin films and investigate their electron transport and emission properties. The ANL team will also work with the ORNL collaborators and R. S. Ruoff at (NW) to grow integrated carbon materials using novel plasma chemistries.
- L.A. Curtiss P. Zapol, and S.R. Phillpot (ANL) will perform computer simulations of UNCD using density functional-based tight binding molecular dynamics to provide information on structure, energy levels and bonding in this material that will be used to help understand its conductivity and field emission properties.
- V.P. Dravid (NW) will perform TEM-based electron holography experiments to study the electron transport and emission properties of carbon materials at the nanoscale.
- R.J. Nemanich (NCSU) will perform PEEM and FEEM studies of nitrogen-doped microcrystalline diamond and UNCD thin films, to understand the relation of the emission sites and the materials properties.

Interactions with DOE Technologies and Industry

The project is relevant to the needs of several DOE Technology Offices, including Defense Programs, EE/Transportation Technologies, and Energy Efficiency. Furthermore, some of the groups involved in the Project are already conducting or discussing joint projects with several companies [e.g., LightWeaver (New Jersey), Flow-Serve (Illinois), Second Sight (California), Raytheon (California), Ionwerks (Texas)] that are interested in the proposed program and in discussing associations to our proposed project.

Management Plan

The Project coordinators will be Drs. D.M. Gruen (ANL) and T.A. Friedmann (SNL). The number of participants and institutions was kept to a manageable level, so that each institution will receive support to allow for either a post-doctoral associate (at the national labs) or a graduate student (at the universities). Thus, we envisage the majority of the funds will be used to support three postdocs and four graduate students, giving the Project a high educational component. Matching funds from the various institutions and possibly industry will help support these postdocs/students as well. The remaining funds will be used to fund an annual Project Workshops and travel costs to major international conferences.

Budget

The following annual budget is proposed, based on $300K/yr funding level

Institution	Funding ($1,000's)	Type of Support
ANL	$65	Postdoc
	15	Graduate Student (Theory)
SNL	65	Postdoc
ORNL	65	Postdoc
LBNL	25	Graduate Student
NW	25	Graduate Student
NCSU	25	Graduate Student
All	15	Annual Workshop (coordinated by ANL/SNL)
TOTAL	$300	

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