

Project Summary: Patterned Graphite Nanoelectronics

The properties of nanoscopic graphitic ribbons are predicted to have much in common with carbon nanotubes. By tailoring their shapes (widths, passivating edge groups, edge roughness, crystallographic orientation) ribbon conductivity can be adjusted from semiconducting to metallic, just like nanotubes. Other properties that graphite ribbons share with nanotubes are (i) size-tunable electronic bandgaps, (ii) chemical robustness, (iii) immunity to electromigration (a major problem in nanoelectronics), (iv) high current capability, and (v) electrically tunable conductivity using the field effect via a proximal gate electrode (“gate-doping”). Just as for carbon nanotubes, carefully-prepared graphite ribbons are also predicted to be quasi-one-dimensional conductors, and possibly room temperature ballistic conductors, properties that would open new possibilities for nanoscale devices. However, in contrast to nanotubes, ribbons of different widths can be seamlessly joined, so that devices consisting of metallic and semiconducting sections can be patterned from a single graphite thin film, without foreign-metal contacts or junctions. This important property provides an easy path to large-scale integration, a goal that nanotube-based devices may never achieve. *Our vision is nothing less than a new form of large-scale integrated electronics based on ultrathin films of lithographically-patterned graphite.*

The first critical steps towards realizing this vision are embodied in a primary goal of this proposal: the development of an all-graphite field-effect transistor (grFET), which in its operation is closely related to the nanotube transistor. The grFET will not only show that robust nanoscale electronics can be realized, but will also blaze a clear path towards large-scale integration of these devices in contrast to nanotube devices.

This important goal will be achieved concurrently and interactively with investigations of fundamental properties of nanoscopic graphite objects. These investigations over a wide range of sizes include electronic and transport properties at ultra-low temperatures ($0.007\text{ K} < T < 300\text{ K}$) and at high magnetic fields ($H \leq 14\text{ T}$), where quantum properties (i.e. quantum dot properties, coherent transport, quantum Hall effect) are most effectively probed.

These investigations will bear out whether room-temperature quantum confinement and ballistic transport can be achieved. This will result in a new class of ballistic transistors and devices based on the discrete electronic states in 2D graphitic quantum dots.

In order to achieve these goals the following research thrusts will be pursued:

1. Production of ultrathin epitaxial graphite films.
2. Production of graphitic nanostructures and devices.
3. Investigations of electronic properties of graphitic nanostructures and devices.
4. Investigations of transport properties of graphitic nanostructures and devices.

The team of Principle Investigators has been chosen carefully to provide complementary expertise and facilities for the project. Preliminary results of the team are encouraging.

Because it can be easily extended to large-scale integration (in contrast to nanotube electronics), the graphite field-effect transistor will rank among the most important achievements in nanoelectronics, possibly outweighing other alternatives such as molecular and nanotube electronics.

2 Introduction

The imminent end of miniaturization of silicon-based electronics due to fundamental properties of the materials involved has led to searches for alternatives. Recently many molecular-based nanoelectronics schemes have been proposed and are being actively pursued. Two of several directions that are seriously pursued are molecular electronics, where the devices are assemblies of molecules, and carbon nanotube electronics.^{42–47} Both these directions derive their properties from conjugated carbon structures.

Key problems facing nanoelectronics with conventional electronic materials are:

1. *Doping*. Statistical fluctuations in the number of dopant atoms become important when the device volume is small.
2. *Electromigration*. Electrical contacts fail due to the unavoidable high current densities.
3. *Lithography*. Materials need to be manipulated and interconnected at the nanometer scale.

In principle, nanotubes provide solutions to the first two problems:

Nanotubes are metals or semiconductors depending only on their geometry and need not be doped.^{48, 49}

Nanotubes can sustain extremely high current densities without degradation.⁴⁴

- Nanotubes are one dimensional ballistic conductors, even at room temperature.^{44,50}

The latter property demonstrates that quantum effects are important and introduces new possibilities for nanoelectronics.

On the other hand, there are serious problems with nanotubes as electronic elements:

- Basic nanotube properties (metal versus semiconductor) depend sensitively on their geometry which current production methods cannot control.^{51,52}
- Nanotubes require nanoscopic metallic contacts which suffer from electromigration and large contact resistances.^{53,54}
- It is entirely unclear how large-scale integration of nanotube devices is to be achieved.

Nanographite structures should retain the advantageous properties of nanotubes as an electronic material and at the same time provide attractive solutions to the problems mentioned above. Moreover, nanopatterned graphite opens the door to a host of novel electronic phenomena.

In particular, nanographite ribbons and devices are predicted to have the following properties:

- electronic structure (semiconductor or conductor) defined by geometry;^{55,56}
- tunable band gaps;^{55,56}
- large current capacity (as for graphite and nanotubes);
- amenable to wafer-scale lithography;
- no metal interconnects required at the device level;
- can be gated via gate structures which may themselves be graphitic;
- should be ballistic conductors^{55–57} (as their nanotube counterparts⁴⁴), which introduces a wealth of device possibilities for both high speed and low power electronics.

Besides ribbons, the properties of graphitic islands^{58–63} add a new dimension to the possibilities. Graphitic islands will have quantum dot properties⁶¹ which manifest quantum mechanical effects even at room temperature.⁶¹

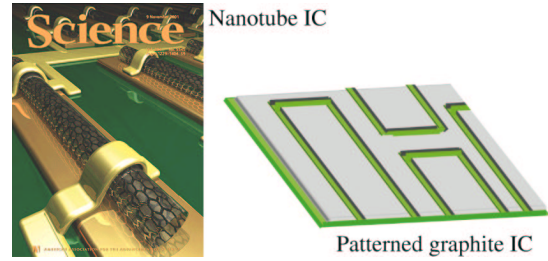


FIG 1: Left: A recent scheme for creating nanotube integrated circuits.⁴⁵ Right: Patterned graphite maintains a planar geometry, with no device-level contacts. The size scale of the patterned features would be ~ 10 nm for room temperature operation.

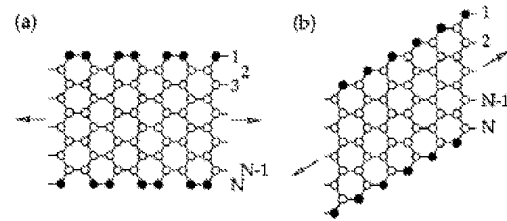


FIG 2: (a) Armchair graphite ribbon (ACGR). (b) Zigzag graphite ribbon (ZZGR). The ZZGR is predicted to be metallic, the ACGR semiconducting or metallic depending on its width (from Ref. 55).

It is telling that there are currently relatively few experimental investigations into the properties of nanostructured graphite^{59,61,64–71} in comparison to the multitudes of investigations on more complex curved nanographitic objects (nanotubes etc.). Hence, experimentally little is known about graphitic nanostructures other than the nanotubes. This is in a large part because graphene ribbons are not as easily produced as nanotubes, but also because of the extraordinary attention that nanotubes have received. It cannot be over-emphasized that there is no fundamental reason to put nanotubes on this pedestal to the exclusion of other graphitic systems, which share many of the properties of nanotubes.

2.1 Electronic properties of graphitic nanostructures

2.1.1 Graphite ribbons

A graphene ribbon^{55,56,72–79} is a ribbon formed of a single layer of hexagonal graphite, while a graphite ribbon (GR) consists of several layers. Figure 2 shows the network and edge structure for GRs extending in the two most

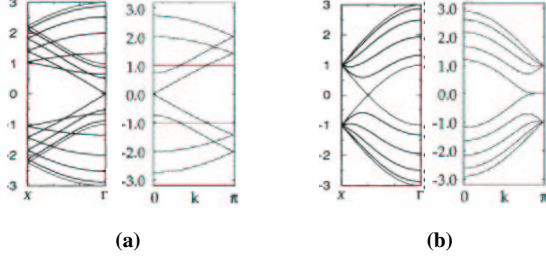


FIG 3: Calculated bandstructures for carbon nanotubes and graphite ribbons. Vertical scales are in eV and horizontal wavevector ranges span the Brillouin zone in each case. (a) Metallic armchair ribbon shown to the right,⁵⁵ nearly analogous metallic nanotube to the left.⁸⁰ Note that the 2 states at E_F , $k = 0$ are present for special ribbon widths, others have a band gap. (b) Metallic zigzag ribbon to the right⁵⁵ and nearly analogous metallic nanotube to the left.⁸⁰

important crystallographic directions. If the edges of the ribbon have a zigzag structure, it is known as a zigzag ribbon (ZZGR). If the edges have an armchair structure it is known as an armchair ribbon (ACGR; note that the terminology refers to the long edges of the ribbons, whereas similar nomenclature for nanotubes refers to the bond geometry around the circumference of the tube).

Similarities to nanotubes. As originally pointed out by Dresselhaus⁵⁵ nanotubes (NTs) and graphene ribbons have much in common. This is clear from the comparison shown in Fig. 3. Both manifest electronic properties due to the confinement of the π electrons by the boundaries imposed by the system. In both cases, the confinement opens a gap at the Fermi level, which closes inversely proportional to the width.⁴⁹ For a nanotube the gap varies approximately as $E_{tube} = 1.2/D$ [eV] where D is the diameter in nm, while for a ribbon $E_{rib} = 1.0/W$ [eV] where W is the width in nm. The electronic properties near the Fermi level of all graphitic systems, and even conjugated molecules, are very well described in a tight-binding approximation which considers only the π orbitals.^{47,56,76–78} This is primarily due to the fact that these orbitals hardly mix with the σ bonds, which in turn are far stronger than the π bonds.⁸¹ Hence even relatively low-level theory reproduces the density of states (DOS) and wave function character for states near E_F , as compared with high-level calculations. For example, a small desktop computer can easily reproduce the published band structures of graphene bands with up to 1000 atoms per unit cell.⁸² Hence, in contrast to most other electronic materials, very large graphitic systems (millions of atoms) can be reliably modeled with state of the art computers.

A very important property of both NTs and GRs is that for certain widths, two 1D subbands span the energy gap giving the structures metallic properties.^{55,56} For nanotubes this occurs when the helicity index (n, m) is such that $n - m$ is a multiple of three.⁴⁹ For ACGRs this occurs when the number of hexagons (aromatic rings) across the width is a multiple of three.⁵⁵ Zigzag ribbons always have two conducting 1D subbands, which asymptotically approach the Fermi level. These bands are associated with the edge states of the ribbon.^{56,60,76,78,83} For ACGRs the two 1D subbands are dispersionless, as they are for metallic NTs. On the other hand, an analysis of the wave functions of the two conducting subbands in the ZZGRs shows that they are localized at the edge atoms only at the 1D Brillouin zone boundary (i.e. for $k_z=1$ in normalized units). They decay exponentially from the edge towards the center of the ribbon with increasing decay length as k_z decreases to $2/3$. For $k_z < 2/3$ the wave function is approximately sinusoidal (1/2-wave with nodes at the edges).⁵⁵

The properties of multiwalled carbon nanotubes closely resemble those of single-walled nanotubes due to the weak interlayer couplings. Similar effects are expected for multilayered graphite ribbons.

Ribbon edges An important difference between NTs and GRs is that GRs have edges. Typically the edges are chemically passivated (by hydrogen for example).^{58,60,69,78,83} Calculations indicate that chemical properties of the passivating groups do not distract from the general electronic structure above (as is found by introducing appropriate on-site potentials at the edges).^{55,78} Passivating atoms or groups may localize carriers or introduce impurity bands, however gap size will generally not be affected. The precise effect is not known a priori however the various possible cases are interesting and can be utilized in nanoelectronic devices. While it is not expected that the passivating groups will significantly change the size of the gap, it may be, that the density of states at E_F , will be affected.

A *rough edge* (a non-ideal edge that can be characterized by additional or fewer hexagons at the edge compared with the ideal AC or ZZ edge) reduces the intensity of the peak in the DOS at the Fermi level, but does not generally open a gap at the Fermi level. Hence even rough edged ZZGRs are conducting. In contrast, theoretically, rough edged ACGRs are generally found to be semiconductors.^{55,82}

Hence, in summary, as for carbon nanotubes, the electronic properties of graphite ribbons are determined by their structure. Band gaps can be tuned from about 1 eV

to 0 eV by changing the width. The conducting and semi-conducting properties can be tailored as well. These are highly desirable properties for nanoelectronics.

2.1.2 Graphite quantum dots

The π electrons will determine the electronic structure of very small single layer and multilayered graphite islands.^{59,61,62,84} The confinement will lead to discrete quantum dot energy states, which can be probed even at room temperature due to the very low density of states at the Fermi level for nanosized objects. These graphitic quantum dots (GQDs) are expected to show interesting properties at low temperatures and high magnetic fields.^{61,62,84} Investigations of the electronic properties of GQDs are invaluable to understand further the properties of ribbons, in particular those with rough edges or those consisting of domains, which may be seen as strings of GQDs.

The properties of GQDs with back gates or side gates will address questions regarding screening effects that are important for graphite nanoelectronics.

2.1.3 Transport properties

Graphene ribbons are expected to show several novel properties like itinerant ferromagnetism,⁸⁵ anomalous temperature dependent magnetic behavior⁸⁶ and zero-conductance resonances.⁸⁶ Like their nanotube counterparts, graphene junctions have been predicted to have device properties,⁵⁶ which is immediately clear from the fact that the electronic properties (semiconducting or metallic) depend on the width.⁵⁵ Hence, appropriately changing the width of the ribbon at the junction forms a semiconducting to metallic junction,⁵⁶ as shown in Fig. 4.

Multiwalled and single-walled carbon nanotubes have been found to be ballistic conductors.^{44,50} Coherent ballistic transport has been demonstrated over many microns in SWNTs^{50,57} and *dissipationless ballistic transport at room temperature* has been demonstrated for MWNTs^{44,57} and nanotube junctions have device properties,⁷⁷ These effects will manifest in graphitic ribbons as well so that complex systems (for example islands and rings contacted with graphitic leads) can be constructed. The coherence will then manifest in mesoscopic transport phenomena⁸⁷ (universal quantum fluctuations, Aharonov-Bohm effect, quantum Hall effect), possibly at high temperatures. The experimental observation of any of these effects will be a spectacular advance for nanoscience.

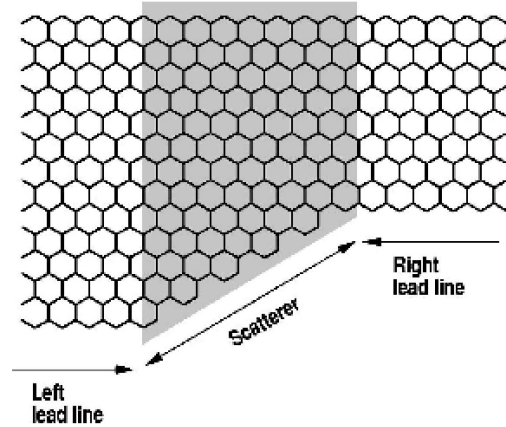


FIG 4: Example of a simple ribbon junction (from Ref. 56). The shaded central region scatters electrons coming into the junction from either of the two graphitic leads.

2.2 Patterned graphite devices

2.2.1 Contacts to graphitic nanostructures

One major consideration and potential advantage of patterned nanographite over carbon nanotubes is related to contacts. It is very difficult to make reliable, low resistance and durable metal contacts to nanotubes.^{53,54} Patterned graphite will not require metal contacts since the contacts themselves are also graphitic.⁵⁶ For example a GR of 10 nm width will (generally) have semiconducting properties, while a GR of 100 nm width will be semimetallic at room temperature. These two structures can be connected seamlessly, so that there is no interface between different materials. This not only makes integration of structures far simpler, it also insures the long-term integrity of the structures. In contrast, the best metal leads to nanotubes are known to fail after relatively short times.⁵³

On the other hand, the metal-graphite interface itself represents an interesting electronic system⁵⁴ due to the large disparity in the characteristics of the electrons (Fermi wavelength and Fermi energy) and dimensionality (2D or 1D versus 3D). The properties of these contacts are essentially unexplored; some inroads into this field have been made recently by two of the PIs (*de Heer, First unpublished data*).

2.2.2 The back-gated graphite transistor.

Nanotube transistors have been fabricated with both single-walled and multiwalled semiconducting carbon nanotubes.^{42,43,45,88,89} The nanotubes were contacted on

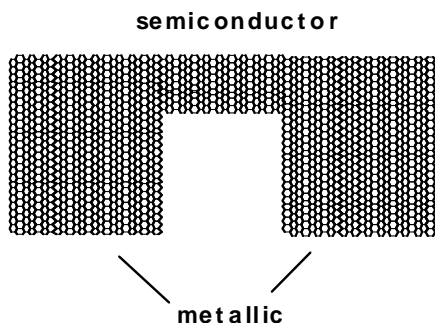


FIG 5: Graphite field-effect transistor (grFET) consisting of a semiconducting graphite ribbon (the channel) connected to metallic graphite leads (source and drain). The structure can have a buried gate or a side gate (a side gate can be patterned directly in the graphite layer).

both sides using lithographically patterned metal contacts. The nanotubes lay over a submerged gate patterned on an oxide-coated silicon wafer. A voltage applied to the gate causes the Fermi level of the tube to shift up or down towards the conduction or valence band (gate doping) which causes the nanotube to conduct, as in a field effect transistor.^{42,43} This achievement was considered to be a breakthrough in nanoelectronics (NY Times, 27 Aug 2001, *IBM Creates a Tiny Circuit Out of Carbon*).

The above analysis indicates that conducting and semi-conducting ribbons can be made by appropriately patterning a graphene sheet and hence graphite ribbon transistors analogous to NT transistors can be produced. However instead of metal contacts, graphite contacts can be made. For example the structure in Fig. 5 represents two conducting graphite leads connected by a semiconducting strip. If this structure is patterned on top of a submerged gate on a SiO₂ substrate (see Fig. 6) then the semiconducting strip will be made conducting by applying a voltage to the gate identical to the gating action accomplished with the nanotube transistor.^{42,43,45,46,52,88-91} Note that the transistor does not require that the edges are perfect (see the previous discussion).

The transistor described above consists of a single layer of graphite. It is likely that multiple layers should function similarly, in analogy to the MWNT transistor.⁸⁹ The criterion is essentially that the fields produced by the back gate can effectively penetrate through the layers. The screening length is not known but it is large since the conductivity perpendicular to the layers is small. This will be investigated empirically. The multilayered transistor has clear advantages since it will have better defect tolerance.

When this transistor is realized it will have enormous advantages over its NT counterpart, since the entire structure is patterned graphite:

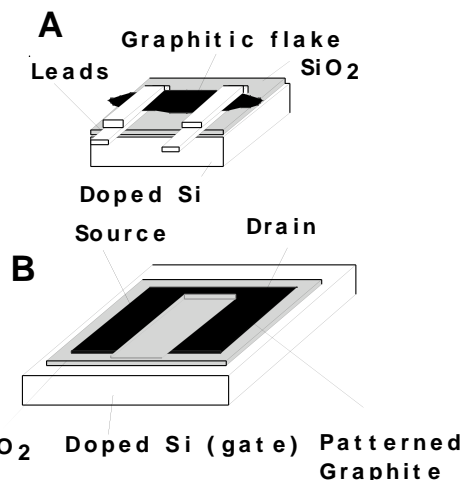


FIG 6: An example of a graphite FET composed of a graphitic flake that is laid down on two prepatterned metallic leads on a SiO₂ substrate over a doped Si back gate. More metal is deposited over the prepatterned ones for better contact. B. FET composed of a patterned ultrathin graphite layer deposited on an SiO₂ layer over a doped Si back gate.

- The structure does not require metal leads;
- The band gap is determined by the ribbon width;
- Perfect lithography is not required since some edge roughness will not interfere with the operation.
- When optimized lithographic methods are developed to pattern the graphite, then extended structures can be produced.
- The durability of graphite compared with the inevitable fragileness of the molecules and contacts with metals will make this technology more important than molecular electronics.

2.2.3 Ballistic devices

The grFET described above closely resemble its silicon microelectronic counterpart, where the source to drain current is modulated by adjusting the Fermi level of the channel. More ambitious devices rely on ballistic transport, which occurs when the electronic mean free path is long compared to the device size. For the very small devices considered here, it is probable that this condition is met even at room temperature, especially considering that ballistic transport on much larger scales are observed in single wall and multiwall carbon nanotubes. If the system is also quantum ballistic (i.e. the electronic coherence

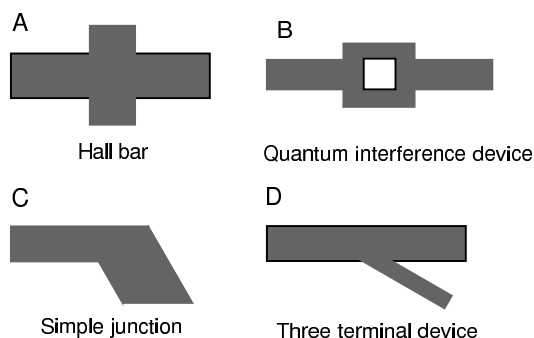


FIG 7: Generic patterned graphite structures. The device structures may be ballistic or diffusive depending on the mean free paths relative to the device size. Ballistic devices rely on phase coherent electron transmission and reflection. A. Hall bar structure (ballistic or diffusive): current flows from left to right and the potential is measured on the top and bottom leads, with a magnetic field applied perpendicular to the structure. B. Quantum interference device. (Ballistic) The current flow through the depends on the magnetic flux through the hole. This device serves as a magnetic field sensor (closely related to the SQUID). C. Simple junction, see also Ref. 56 Transmission through the junction is determined by the geometry of the junction. D. Generic three terminal device. The junction region is patterned so that it is semiconducting, while the leads are ballistic conductors. Applying a potential to the bottom lead affects the Schottky barrier at the junction and hence acts upon the electronic transmission through the device (see also Refs. 56 and 77).

length is longer than the device size), then quantum interference effects will be important for the transmission,^{50,87} which opens up an entirely new paradigm for nanoelectronics. Examples of ballistic devices are the quantum interference device (QID), which is closely related to the SQUID. In this device (see Fig. 7), the electrons can take two paths from the left terminal to the right terminal, i.e. either over the hole or under the hole. These two paths will interfere with each other depending on the relative phases of the wavefunctions of the two paths. This in turn depends on the magnetic flux through the hole. Hence this device functions as a sensitive magnetic field sensor. Three terminal ballistic transistor devices (see Fig. 7D) rely on the effect that the back scattering of electrons that pass through the structure depends on the potential profile in the junction. There are several possible schemes to influence this potential. One is to construct a control lead that is coupled to the junction via a Schottky barrier, (by appropriately patterning the junction, see Ref. 56). A voltage applied to the control lead will enhance or reduce the transmission through the device, which hence functions as

a ballistic transistor.

3 Projects

The patterned graphite nanoelectronics program breaks down into distinct projects. Aspects of each can be conducted in parallel. The four areas are:

1. Production of ultra-thin graphite films.
2. Production of graphitic nanostructures and devices.
3. Investigations of the electronic properties of graphitic nanostructures and devices.
4. Investigations of the transport properties of graphitic nanostructures and devices.

3.1 Production of ultra-thin graphite films (Erbil, First, Wang)

The key to the development of large-scale integrated graphite nanoelectronics is the ready availability of single-crystal graphite films having thicknesses in the range of 1–30 graphene layers. Currently, it is impossible to grow large bulk crystals of graphite. Some preliminary experiments have demonstrated the feasibility of growing ultra-thin graphite layers on transition metals and carbides by the chemical vapor deposition (CVD) technique.^{92–94} However, the growth of ultra-thin single-crystal graphite layers on *insulating* substrates is essential for the development of graphite nanoelectronics.

The goal of this part of the proposed program is to grow epitaxial graphite layers on commonly available insulating substrates or buffer layers by using the CVD technique. The growth process should produce films for initial scientific investigations as well as for large-scale device production in the future. In the CVD technique, a carbon-bearing compound is transported to the reaction zone and the formation of graphite occurs via the pyrolysis of the precursor on a surface. This process can take place catalytically in the temperature range of 700–1000 C. If the lattice match and the surface energies are compatible, the film will grow epitaxially on the substrate. During the life of the program, a close coupling will be maintained between film growth and materials characterization efforts.

We will particularly investigate three different approaches for the development of epitaxial graphite layers on insulating surfaces:

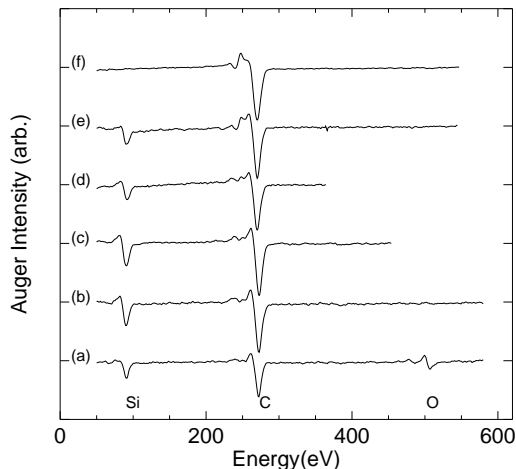


FIG 8: Auger spectra for successively higher flash-anneal temperatures of SiC(0001). (a) 950°C, (b) 1250°C, (c) 1350°C, (d) 1450°C (e) 1500°C (f) > 1500°C. The data show that oxygen can be controllably removed (as SiO), followed by Si. Note the evolution of fine structure in the carbon peak as the Si/C ratio decreases (c–f). Data acquired recently by Erbil and First.

3.1.1 Outdiffusion and CVD growth on SiC

Direct deposition of a single-crystal graphite film on the carbon surface of 6H-SiC(0001) by CVD. SiC is a wide bandgap (3 eV) semiconductor and has a good lattice match with a high order coincidence lattice.⁹⁵ SiC layer also can be grown as a buffer layer on a Si(111) wafer followed by the deposition of graphite film.

3.1.2 CVD growth on h-BN

Deposition of a single crystal graphite film on h-BN buffer layers grown on 6H-SiC surface. h-BN has a hexagonal layered structure with a band gap of 6 eV and a lattice mismatch less than 2%.

3.1.3 CVD growth on Ni/Si(111)

Deposition of graphite layer on nickel-coated silicon substrate. A thin oxide layer on the silicon wafer will be provided to slow the diffusion of nickel into the substrate⁹⁶ during the growth of the graphite layer. After the growth of the layer, a high temperature anneal will be performed to diffuse nickel into the silicon substrate. In this approach, we expect to produce films having crystallites with c-planes parallel to the substrate surface but there may not be in-plane order between the grains.

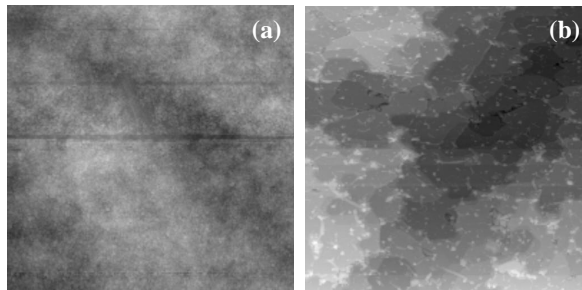


FIG 9: First attempt at graphitizing SiC (with imperfect temperature control). (a) 200x200 nm STM image of SiC after removing oxygen (see Fig. 8b). (b) 200x200 nm STM image of graphitized SiC (see Fig. 8f). Flat regions in (b) show graphite atomic structure in high-resolution images. Gray scales span 8 nm in each image. Data acquired recently by First.

The graphite films grown will be provided to the other members of the team for further physical property evaluation and device fabrication.

3.2 Production of graphitic nanostructures

Graphitic nanostructures can be formed in a variety of ways. The preferable method is lithographic patterning of deposited thin layers of graphite or graphene (see 3.1). The second method more closely resembles current nanotube technology, and relies on manipulation of self-assembled graphitic nanostructures. The graphitic nanostructures described below will be produced in the laboratories of ZL Wang, W de Heer, P. First and A Marchenkov

3.2.1 Lithographic patterning of graphitic nanostructures (Berger, de Heer, Marchenkov, First, Wang)

SPM lithography. This method will be used in order to demonstrate a working transistor prototype. Thin graphite platelets (micron sized) are formed by etching graphite as has been demonstrated by Ruoff⁹⁷ using the reactive ion etching process on graphite (Fig. 10). In addition, production of carbon ribbons by evaporation from a silicon carbide (SiC) electrode was demonstrated⁹⁸ (Fig. 14). These ribbons might provide an attractive alternative to platelets. The graphite platelets/ribbons are transferred to a suitable substrate (for example oxidized doped device grade silicon). The silicon wafer serves as the gate electrode. Nanoscopic patterns will be cut on these platelets using electrochemical SPM lithography. This method has been successfully applied to HOPG at our facilities by Berger following the procedure developed by McCarly et

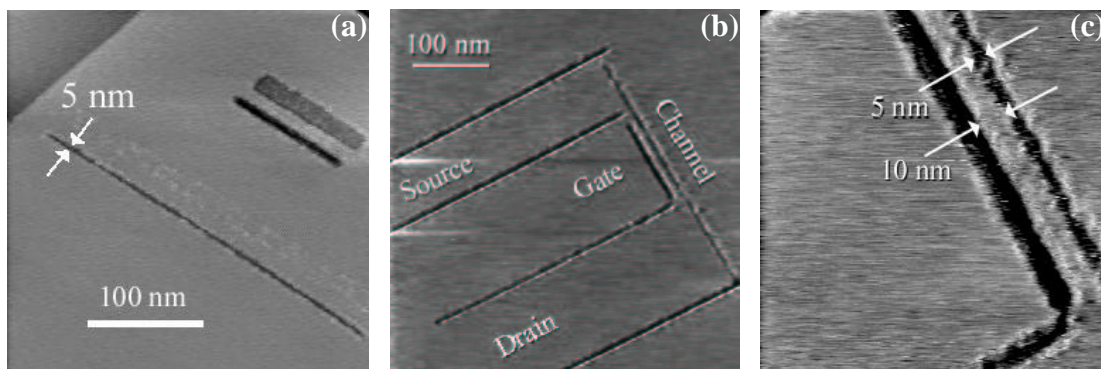


FIG 11: Examples of STM lithography on graphite. The techniques were developed very recently in our lab, following Refs. 100 and 99. (a) The three lines shown here show excellent control on width and line uniformity. (b) A patterned structure on HOPG which closely resembles ultimate side- and back-gated grFET structures. (c) Closeup of lower right-hand corner of the gate structure in (b)

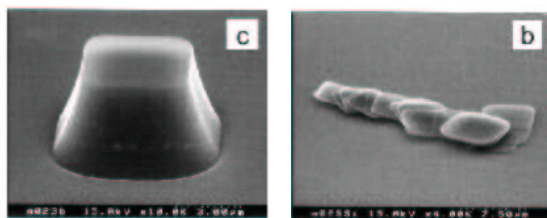


FIG 10: Left: SEM images of graphite tower created by oxygen plasma etching on an HOPG substrate. Right: SEM images of graphite platelets from tower deposited on a Si(001) substrate.⁹⁷

al.⁹⁹ and Penner et al.¹⁰⁰ to produce truly impressive nanometer-sized patterns on HOPG. Feature sizes on the order of 10 nm with lines up to 300 nm long are reliably produced (Fig. 11). The Park Autoprobe SPM apparatus (see Facilities) is designed for SPM lithography. The source and drain electrodes can be produced by two methods:

1. An individual appropriate graphite platelet⁹⁷ will be located on the wafer and etched to the desired shape. Subsequently, leads will be added by evaporation methods to make contact to the graphite islands, which make the source and the drain similar to the methods to produce nanotube transistors⁸⁸ (Fig. 6).
2. Alternatively, an array of source and drain electrodes can be initially patterned on top of the SiO₂ insulating layer with the separation slightly smaller than the typical platelet size (Fig. 6a). A platelet can then be caught electrostatically to span the gap between the electrodes in a fashion similar to trapping metallic clusters and organic molecules. Subsequently, an additional layer of metal will be deposited on top of

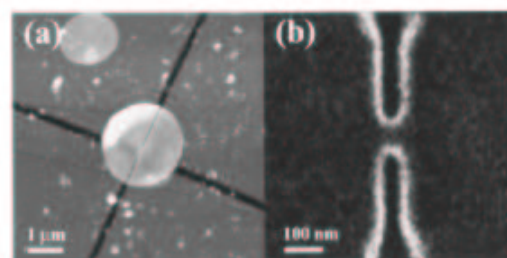


FIG 12: (a) AFM image of a 50 nm wide constriction cut into a 2.0 mm graphitic disk connected by four flat gold electrodes, which are separated by 150 nm wide grooves. (b) Detailed FIB image of a 40 × 70 nm constriction cut into a graphitic disk. (from Ref. 64).

the existing electrode pattern to insure a reliable contact between graphite and electrodes. This method has the advantage of producing multiple samples on a single wafer in well-defined positions. The platelet shape can be modified subsequent to the electrode production.

Focused ion beam lithography. Focused ion beam (FIB) lithography has been successfully applied to thin graphitic structures. With this method lines have been cut in thin graphite islands with a precision of several nanometers.⁶⁴ Structures of virtually any shape can be cut this way. Furthermore, the method allows gold electrodes to be patterned by decomposing organometallics with the FIB. This method has successfully applied by Ebbesen who produced a 50 nm wide 50 nm wide graphite ribbon which connects two larger graphite islands⁶⁴ (see Figs. 12 and 13). *Marchenkov* will perform the FIB lithography at the NSF-sponsored National Nanofabrica-

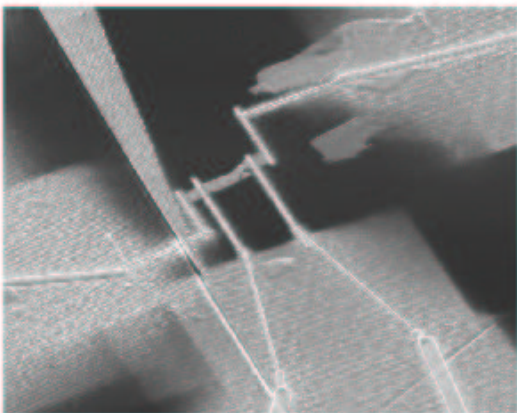


FIG 13: AFM image of a 4 electrodes system on a small graphene tape of around 2 sheets thickness and 100 nm width (F. Armand, M. Normand, V. Huc T. Ebbesen, H. Lezec¹⁰¹).

tion Network facilities. Note that the Georgia Tech Center for Nanoscience and Nanotechnology (under the direction of Wang) is in the process of acquiring a FIB lithographer.

Electron beam lithography. E-beam lithography methods will be used in order to produce and pattern a desirable electrode pattern on silicon and silicon carbide wafers, using standard methods.

In addition, conventional e-beam lithography methods will be attempted at the later stages of the project to fabricate integrated circuits (IC) out of thin graphite films deposited on top of appropriate insulating substrates. Two approaches can be envisaged here, depending on the quality and subsequent treatment of the carbon film produced by the deposition on a wafer of Si or SiC.⁹⁵

1. The desired IC pattern can be obtained on a layer of photoresist deposited on top of a thin uniform graphite layer. The IC is then obtained by a combination of standard developing and dry-etching steps.
2. The desired IC pattern will be formed in a layer of photoresist on top of the substrate appropriate for the subsequent graphite deposition. After graphitization, the photoresist and graphite deposited on top of it can be removed by standard techniques.

The School of Physics is in the process of setting up an e-beam lithography facility that will be on-line in January 2002 under the supervision of Marchenkov.

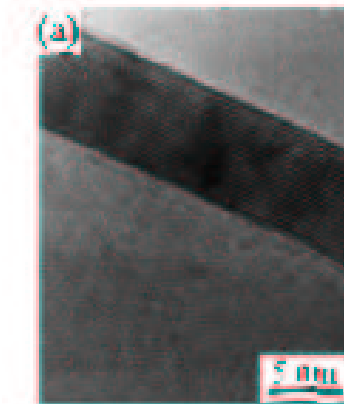


FIG 14: Graphite ribbon produced by a carbon arc in a hydrogen atmosphere.

Dip pen lithography. Dip pen lithography has recently been developed by Mirken and co-workers.¹⁰² This experimental method uses an ambient scanning force microscope (for example the Park Instruments CP unit). The tip is used as a dip pen where the pen is first coated with a layer of water-soluble molecules which are transferred to the substrate when the tip writes over the substrate. In this way lines as narrow as 15 nm have been written both on metal as well as on semiconducting substrates. For these purposes molecules will be transferred to metal and semiconducting substrates. These molecules can be polymerized by chemical treatment or graphitized (for example by heating or e-beam illumination). Alternatively organometallic molecules deposited on the non-conducting substrate can be patterned with dip pen lithography to produce metallic lines. Two AFMs (one in WdH's lab and another in ZL Wang's lab) are suitable for this project.

3.2.2 Self assembly methods (de Heer, Wang, Erbil)

Arc produced graphite ribbons. Graphite ribbons have been produced in carbon arcs very similar to those used to produce nanotubes as shown in Ref. 98. The arc is struck in a hydrogen atmosphere and the electrodes are impregnated with SiC (Fig. 14). This process produces well formed graphite ribbons that can be harvested and manipulated similar to the methods developed for nanotubes. This process will be invaluable to demonstrate the properties of graphite ribbons and to produce prototype devices (closely paralleling the nanotube transistor development).⁴²

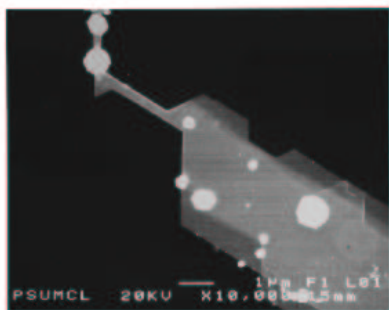


FIG 15: Secondary electron image of a graphite ribbon and diamond crystals nucleated on it. (from Ref. 103).

Microwave-plasma chemical vapor deposition.

Nickel-assisted microwave CVD in a hydrogen plasma has been applied to produce impressive freestanding crystalline GRs (several 10s of nm wide and thick) by R. Roy et al.¹⁰³ (Fig. 15). These can be harvested and deposited on suitable substrates after which contacts can be applied using standard e-beam lithography methods (as is currently done with NTs).⁴² Initial studies will involve obtaining material from Roy et al.¹⁰³ If this direction proves to be promising then it will be aggressively pursued and the Georgia Tech Nanotechnology Center (ZL Wang) will purchase the necessary equipment.

Etchpits in HOPG. Etch pits form in HOPG when it is heated in air.^{69,104,105} The depth and diameter of the pits can be controlled to a reasonable degree by adjusting the temperature.¹⁰⁴ These holes occur at defects in the HOPG. When two etchpits nearly meet a narrow strip remains. This method is not appropriate to produce predetermined graphite patterns however it is a simple and well established way to produce a variety of well graphitized samples for investigations of the properties of low dimensional graphitic objects like islands and strips.

This technique has been successfully applied in *de Heer's* lab and imaged by *First* (Fig. 16).

Arc produced nanoparticles Small faceted graphitic particles ($\approx 5\text{-}50$ nm) are abundantly produced in carbon arcs.¹⁰⁶ The particles are suspended in ethanol (using ultrasonic dispersion method) and dried on a substrate. WdH has extensive experience in the production of these nanoparticles.

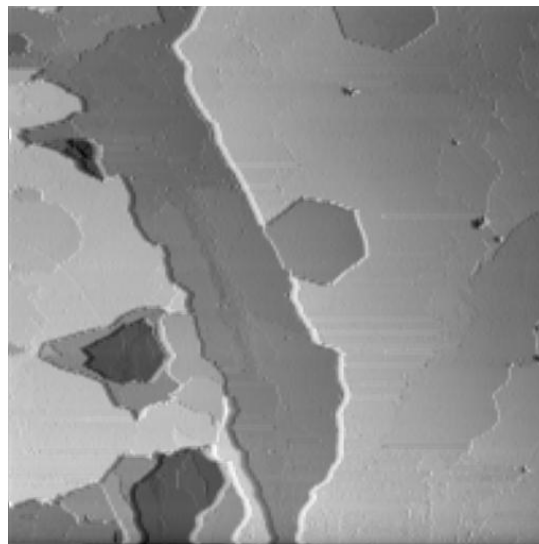


FIG 16: STM image of etch pits formed in HOPG by heating in atmosphere to 650°C . Image size $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$.

3.2.3 Structural characterization (*Wang, First, de Heer*)

The patterned graphitic structures will be characterized at the Georgia Tech electron microscopy facility. The Georgia Tech electron microscopy center has the instruments and the expertise for detailed chemical and structural characterization of the nanostructures that are produced by the methods described above. Further characterization will be performed with SPM (in air by WdH, in UHV by PF, in HV by ZLW).

3.3 Electronic properties of graphitic nanostructures & devices (*First, de Heer*)

In this project, the properties of graphene and graphite islands and ribbons will be investigated using scanning tunneling microscopy (STM) and spectroscopy (STS) in ultrahigh vacuum from 4K to 300 K and in magnetic fields up to 8 T (see Facilities). These experiments will probe the density of states (DOS) of the graphitic structures on the atomic scale. The DOS near the Fermi level will reveal directly the metallic or semiconducting nature of graphite ribbons and islands.

Investigations will begin with STS measurements of graphite steps, ribbons, and islands that occur naturally on HOPG surfaces (or ultrathin graphite films) fired in oxygen or similar atmospheres (see Sec. 3.2.2). Other self-assembled or lithographically-defined nanostructures will

be studied as they become available. Due to the poor transport between graphite layers, we expect that armchair ribbons should show a distinct gap around E_F , even on the extended graphite substrate. Zigzag ribbons are expected to have a unique topological edge state at E_F (evidence already exists^{67,69}) that could give rise to ballistic conduction. Maps of the spatial distribution of this state across the ribbon will be compared with calculations. For both ribbon types, we will determine experimentally the change of electronic structure with ribbon width, the effects of edge roughness and the sensitivity of the electronic structure to passivating edge groups. The effect of high magnetic fields on the ribbons (which may undergo an electronic phase transition in high fields) also will be probed.

Graphitic islands will be studied by STS concurrently with the graphite ribbons. In this case we expect that quantum dot properties will be observable at cryogenic temperatures, and perhaps higher. Energy-resolved DOS maps will be acquired in order to compare the wavefunction distribution with calculations (see also Sec. 5.3).

Patterned graphite devices can also be investigated via STM and STS. The low-temperature STM described under Facilities has connections for up to 4 contacts to the sample, sufficient for biasing many basic devices. Additionally, the sample can be positioned anywhere within a 5mm diameter circle with a ~ 10 nm minimum step. This will allow nanoscale devices to be located, provided directional and identification marks are included in the lithography (the scanning range is $1.2 \mu\text{m}$ at 4 K).

In order to study the effects of gate-doping and electrostatic screening, potentials will be applied to electronic gates beneath or to the side of ribbons/islands. Such experiments (and even those mentioned previously) must properly account for the influence of the electrostatic field of the STM tip, somewhat analogous to the tip-induced band-bending on semiconductor samples.¹⁰⁷ The tip-field itself could be used to gate an operating grFET at selected positions along the channel. The effect on the source-drain current would provide more information on the local electronic structure along the channel (see also Sec. 3.4).

The properties of metal contacts (contact resistances and non-linear transport) and the electronic structure near metal islands on HOPG will be measured. Preliminary experiments (*First, de Heer*) have demonstrated important effects (high contact resistances, dramatically nonlinear dependence on contact area, and non-ohmic transport at high bias voltages).

3.4 Transport properties of graphitic nanostructures & devices (*Marchenkov, de Heer, Berger, First*)

A broad range of remarkable physical phenomena have been revealed through transport studies of electrons constrained to quasi two-dimensional sheets at low temperatures. For example, in the presence of intense magnetic fields, these 2D electron gases exhibit quantization of the Hall voltage to levels determined only by fundamental physical constants. Under these conditions, electrons do not exist in simple plane-wave states, but are arranged in Landau levels. The Quantum Hall Effect (QHE) is the direct consequence of the nature of these states in two dimensions. At even higher magnetic fields, the electrons further condense into unique many-body correlated states which occur at rational fractional filling $\nu = p/q$ of Landau levels (Fractional Quantum Hall Effect).

A variety of different topological 2D electron structures with nearly atomic resolution can be manufactured from graphite ribbons, sheets or films using either lithographic, or STM-based techniques. Examples include (Fig. 7) a Hall bar (QHE regime), a mesoscopic interferometer, a ribbon knee junction⁵⁶ (see also Fig. 4), and an asymmetric Y-junction, analogous to the nanotube case.⁷⁷

Due to the presence of the morphological edges, graphitic ribbons add a remarkable twist to the multitude of electron transport phenomena studied in carbon nanotubes as well as other low-dimensional electron gases. Theoretical analysis⁵⁶ has shown that the conductance of graphite nanoribbons as well as that of the ribbon junctions crucially depends on their morphology as well as edge shapes. *Marchenkov's* group has capabilities to study electron transport phenomena on patterned structures at temperatures from 0.007 K to 300 K in the fields up to 9 Tesla (14 T with flux concentrator), which will provide detailed information on the nature of the carriers and other mesoscopic transport properties. Initially, various samples will be tested to determine the relation between the conductivity the morphology of the ribbon (width, aspect ratio, edge shape and roughness). Ribbon morphology will be determined using optical, electron, and scanned-probe microscopy methods as described above. Many of the graphite films produced at Georgia Tech will be sent to *Berger* at CNRS, who has facilities and expertise in materials characterization via transport measurements and electron spectroscopies.

Based on the energy scaling described in Sec. 2, graphite ribbons several nanometers in width are expected to show ballistic and quantum effects at room temperature. However, it is important to realize that low-temperature transport measurements will be essential for at least three

reasons: 1) Characterization of material quality, 2) Fundamental measurements of electronic structure and electron-correlation effects, and 3) Low temperatures extend the size range at which ballistic and quantum effects can be observed. For the graphite structures of interest, it should be possible to observe the basic properties and device operation for ribbons tens of microns wide at the lowest temperatures. This reduces the patterning constraints to the level of optical lithography. Furthermore, high quality single-crystals of graphite are available in mm sizes (Kish graphite). Consequently low-temperature device measurements could begin immediately, independent of progress in the other project areas.

Low temperature measurements (4K) on these structures using STM methods will be carried out by *First* as previously described. Measurements of this kind have been particularly useful to characterize transport in contacted nanotubes and will do so for nanoribbons as well. It also may be possible to use the STM to do local null-current potentiometry (in the manner of a Kelvin probe) in order to map the distribution of QHE edge states.¹⁰⁸

4 Education

Scientists educated through undergraduate, graduate, and post-graduate research constitute the most important means of technology transfer from universities to industry. Six Ph.D. students, 5 undergraduates, and 2 postdocs will be supported directly through this grant or associated cost-sharing. Their training is clearly the most direct benefit of this funding. However, all levels of education will benefit from the requested funds. In particular, we have noted a significant weakness in many graduate programs: stagnant Masters degree curricula. With partial support from this new funding and industrial sponsors, we hope to address this issue.

K-12 Education: Through the requested funding, the PIs will support K-12 education in several ways: 1) Through participation in the Georgia Industrial Fellowships for Teachers (GIFT) program (www.ceismc.gatech.edu/ceismc/programs/gift/homepg.htm) GIFT arranges summer fellowships for K-12 math and science teachers at several leading businesses and public science organizations (including Georgia Tech). The program is administered by the Georgia Tech College of Sciences' Center for Education Integrating Science, Mathematics and Computing (CEISMC). Last year, 80 teachers were granted fellowships throughout the state. 2) Through participation in the educational programs of the Georgia Tech Center for Nanoscience and Nanotechnology that has been established recently (Z.-L. Wang,

Director). The new Center will establish a "Research Experiences for Teachers" program similar to GIFT, in addition to outreach programs. 3) Through less formal but more direct contact with K-12 students. Examples from the PIs experience in recent years include participation in "Science and Technology" nights at local schools, hosting lab visits for K-12 classes, loaning equipment or materials to the local science museum, etc.

Undergraduate Education: Funds to support 5 undergraduates per year have been requested specifically for the purpose of enhancing research opportunities for undergraduates. Students will work in conjunction with graduate students and postdocs on the projects described previously. Our goal is to have a student participate for at least 1 year in the research program. This is enough time for a good student to make a real contribution, and it is a sufficient basis for an advisor to write a meaningful letter of reference for graduate schools. The PIs will also continue to participate in the NSF-sponsored Research Experience for Undergraduates (REU) program administered through the School of Physics (J. L. Gole, PI). In this program, undergraduate students from around the country participate in full-time research for one summer.

Graduate Education: In the past 20 years or so, the rate at which fundamental discoveries appear in technological innovations seems to have increased. One oft-cited example is the phenomenon of "giant magnetoresistance," which went from discovery to computer hard-drives in about 7 years. This is not much more than one generation of Ph.D. students. There is a need for technology transfer and training on a time scale shorter than can be accommodated through Ph.D. research, yet with more depth than is possible at the undergraduate level. Vibrant Masters degree programs could help substantially.

We propose to develop a new Masters degree specialization: "Science at the Nanometer Scale," to be offered through the Schools of Physics, Chemistry, and Materials Sciences and Engineering. Furthermore, we hope to secure industrial sponsorship of graduate fellowships specifically for Masters study in this field. The degree program would consist of at least two special interdisciplinary courses (also open to Ph.D. students) and 1 year of focussed thesis research, in addition to selected graduate courses in the student's home department. The specialty courses will cover 1) the basic physics and chemistry of nanometer-scale structures, 2) the synthesis and characterization of such structures, and 3) present and future applications of nanoscale materials and devices. These courses will draw heavily from examples in the current literature. They will be integrated with the graduate curricula cur-

rently under development in the Georgia Tech Center for Nanoscience and Nanotechnology.

5 Organization and management

5.1 Interdisciplinary research team

The Interdisciplinary team is constructed of five carefully selected PIs with diverse and complementary areas of expertise (see below). Accordingly, in broad strokes the project is subdivided into five areas and two categories.

The basic science category involves the fundamental electronic and transport properties of nanoscale graphite systems (*First* and *Marchenkov*). The applied category involves the construction of lithographically patterned devices and production of epitaxial graphite films (*de Heer*, *Erbil*). *Wang* will accomplish various levels of characterization.

One graduate student, one undergraduate student and one post-doc will assist each PI. A sixth graduate student, supported by Georgia Tech cost-sharing, will work with *de Heer* on development of the grFET. Two postdocs (#1, #2) will be involved who will interact with several groups. This insures cohesion in the efforts.

Walt de Heer (Project Director)

Transistor development

Ambient AFM, STM; lithography; transport.

Postdoc#1; 2 graduate; 1 undergraduate.

Phillip First

Electronic and structural properties of islands and ribbons

UHV STM, STS; cryogenic STM, STS.

Postdoc#2; 1 graduate; 1 undergraduate.

Alexei Marchenkov

Mesoscopic transport properties in nanographitic structures; lithography

Dilution refrigerator methods; Ultralow temperatures, High magnetic fields; e-beam lithography.

Postdoc#2; 1 graduate; 1 undergraduate.

Ahmet Erbil

Graphite ultrathin-film development

Epitaxial graphite film growth, chemical vapor deposition.

Postdoc#1; 1 graduate; 1 undergraduate.

Zhong Lin Wang

Characterization of nanographitic structures

Electron microscopy methods; STM.

Postdoc#1; 1 graduate; 1 undergraduate

De Heer has extensive experience in the properties of carbon nanotubes and carbon onions (field emission,^{2, 109–112}

ballistic conduction,^{9, 44, 113} mechanical properties,^{5, 8, 114} electronic, magnetic, and chemical properties,^{115–121} production^{122–127}), which are closely related to the graphitic nanostructures proposed here. In conjunction with senior collaborator **Claire Berger** (CNRS, Grenoble, France; sabbatical at Georgia Tech through 2002), he is developing lithography methods for graphitic material using STM. *de Heer* has collaborated closely with *Wang* for the past three years on nanotube related projects. This collaboration has resulted in several important papers on the subject.

First has extensive experience in measurements of the electronic properties of nanoscopic systems and surfaces using ultra-high vacuum and low-temperature scanning tunneling microscopy methods (STM/STS, BEEM/BEES). These methods are crucial to examine the local density of states of the graphitic ribbons and islands, which reflects the location of the Fermi level, the metallic character, the size of the semiconducting gap, the effect of the edges (i.e. the predicted peak in the DOS at E_F) and edge roughness, the effect of the number of layers, etc.

Marchenkov has extensive experience in transport measurements on nanoscopic systems at ultralow temperatures. At these low temperatures quantum effects can be efficiently probed for level spacing as small as several tens of microvolts. Interesting and exotic two-dimensional mesoscopic electronic effects, (ballistic conductance, quantum Hall effect) can be probed. *Marchenkov* also has experience in nanofabrication methods including e-beam lithography. He is co-director of the new Nanofabrication Facility in the School of Physics at Georgia Tech.

Erbil has extensive experience in the fabrication and study of novel thin film materials, including ferroelectrics, silicon, II-IV and II-VI semiconductor compounds, transition metal oxides, high-temperature superconductors and diamond. Much of his expertise would ordinarily be found in a chemical engineering department. He holds five patents in the field of CVD chemicals and thin film production. He is the founder and president of Quantek Materials, Inc. He obtained his PhD at MIT with M. Dresselhaus, where he worked on intercalated graphite materials.

Wang is the director of the Georgia Tech Center for Nanoscience and Nanotechnology and the director of the electron microscopy facility. He has collaborated intensively with *de Heer* (see above) on several important nanotube related projects. His experience in electron microscopic characterization of materials is invaluable for the project. The Center is in the process of acquiring a FIB lithographer, which is required for the project.

5.2 Team coordination

Area leaders are designated above. Interactions will be largely informal, since the collaborators are presently all within walking distance of one another. This will change when *Berger* returns to CNRS (Grenoble, France) at the end of 2002. Overseas contact will be mostly through email for information exchange, and express mail for sample exchange, with telephone (or netphone) calls when necessary. Additional funds will be sought to expand this partnership (see Sec. 5.3).

Monthly meetings of all Georgia Tech team members will be held to promote interactions and to give students an opportunity to present new research results. Such presentations are an important part of graduate (and undergraduate) education, yet often the number of opportunities is limited. We anticipate that each meeting would have one 30 minute talk by one of the students, with brief summaries of progress in each area from the others, and a discussion of proposed work for the next month. *Berger* will provide input before the meeting to other team members, and will be given a meeting summary afterwards. We will also attempt to use internet video collaboration methods (e.g. CUseeMe) to include *Berger* in the discussions more directly.

The five PIs will meet each semester (including summer) to discuss student support and large expenditures. Funds distribution will be approximately as indicated in the Budget Justification, but large purchases will be subject to approval of the Project Director (*de Heer*). In order to maintain some flexibility in the budget, yet avoid micromanagement, each PI will be allowed full control over a percentage (perhaps 70%; to be determined on a yearly basis by the Project Director and co-PIs) of their allocation shown in the Budget. Allocations in excess of this amount would require approval of the Project Director, with input from the co-PIs.

5.3 Additional collaborations

The present work forms the scientific basis for numerous potential applications and further fundamental studies. It is the start of an entirely new field. In order to facilitate expansion of this field and ultimately to create economic benefit, several additional collaborations will be forthcoming, as described below. The present partnership with CNRS will be continued and expanded, hopefully through supplemental funds from NSF that target international opportunities (as described in the program solicitation).

We anticipate expansion of the program in two directions: 1) towards fundamental properties of the 2D electron gas in graphitic nanostructures, and 2) towards large-

scale integrated circuits composed of patterned graphite devices. Georgia Tech has local expertise in both directions, and joint projects will be sought after the initial results from the work proposed here. Please see letters in the Supporting Documents section of this proposal.

5.3.1 Fundamental properties

Prof. *Uzi Landman* has taken an active interest in the projects proposed here. He and his Center for Computational Materials Science are uniquely qualified to model many the properties that are the subject of investigation here. His broad experience in modeling transport in low dimensional systems (metal and semiconductor nanowires; semiconductor to metal junctions¹²⁸) as well as correlation effects in low electronic density quantum dots,¹²⁹ will guarantee first-class theoretical support in the various scientific directions proposed here. It is particularly noteworthy that Landman's Center for Computational Materials Science is renowned for providing properties predictions of realistic systems.

5.3.2 Large-scale integration

The full economic value of this research will only be realized when these graphite structures are formed into practical integrated electronic devices. To accomplish this, the structures must be *a)* accurately modelled and optimized, *b)* integrated on the giga- to tera-scale, and *c)* usefully packaged.

Prof. *T. K. Gaylord* (ECE) has developed modelling and optimization techniques for 2D ballistic devices.^{130–133} His expertise will be invaluable for implementing practical devices, especially multi-terminal diffractive devices. Prof. *James Meindl* (ECE, Director of Microelectronics Research Center) is known as a world-leader in microelectronics, with particular interests and expertise in giga-scale integration.^{134–137} The resources of the NSF-sponsored *Packaging Research Center* at Georgia Tech will also be available for the last crucial step in creating a marketable integrated circuit.

5.4 Schedule

The schedule of the project is outlined below, subject to modification depending on the actual progress and findings.

Year1

- STM based nanolithography on HOPG, arc production of graphite ribbons; (WDH)

- UHV STM of graphitic nanostructures (steps and islands on HOPG, etch-pits, graphitic particles, arc produced graphite ribbons); graphite layers on SiC (PF)
- E-beam lithography of graphitic nanosystems; defined leads on arc produced graphite ribbons (AM)
- Epitaxial graphite films on metals; epitaxial graphite films on SiC (AE);
- TEM, SEM characterization of graphitic nanostructures produced by AE, WDH, PF; (ZLW)

Year 2

- STM based nanolithography on HOPG (continued), on epitaxial films on metals; and on epitaxial films on SiC ; arc production of graphite ribbons (continued); (WDH);
- UHV STM of lithographically patterned graphitic nanostructures; graphite layers on SiC (PF)
- Ultra low temperature transport on contacted graphite ribbons; patterned doping of SiC and other semiconductors to produce back gate structures; (AM)
- Epitaxial graphite films on semiconductors (AE); Metal assisted microwave CVD methods for film growth.
- TEM, SEM characterization of graphitic nanostructures produced by AE, WDH, PF; (ZLW)

Year 3

- STM lithography on back gate patterned graphite films; development of side-gate transistor (WDH);
- UHV STM,STS of lithographically patterned graphitic nanostructures; Effects of shape on DOS; effect of passivating atoms/molecules on DOS; (PF)
- Ultra low temperature transport on contacted back-gated and side-gated structures (AM)
- Epitaxial graphite films on semiconductors with patterned back gate doping (AE);
- TEM, SEM characterization of graphitic nanostructures produced by AE, WDH, PF; (ZLW)

Year 4

- Production of integrated nanographite device (at least two active elements, back-gated or side gated), using previously developed STM patterning methods (WDH)
- UHV STM, STS of prototype devices; High field effects; Quantum dot effects; Low temperature effects (PF)
- Ultra low temperature transport of patterned devices (AM)
- Improvement of epitaxial film quality and developments for mass production (AE);
- TEM, SEM characterization of graphitic nanostructures; (ZLW)

6 Conclusion

In conclusion, the projects outlined here will make important inroads into the area of nanographite science and engineering. The proposal is broad-scoped and involves overlapping areas of fundamental properties and device design.

The fundamental properties of nanoscopic graphite are investigated as a function of size, shape, temperature and fields. Nanotubes have demonstrated that quantum effects in nanographite systems are important, due to confinement and the low density of states at the Fermi energy. Electronic confinement in low dimensional systems (an important current field of research) gives rise the quantum Hall effect, ballistic transport, and correlated electronic effects (Luttinger liquids in ribbons, super-atoms in quantum dots). Electronic quantum properties are reflected in nanographite ribbons when kT is smaller than the bandgap (*cf.* nanotubes) which will manifest themselves, even for relatively wide ribbons (up to 50 nm) at room temperature. Initial nanographite electronic device structures are closely modeled after their nanotube counterparts to produce back- and side-gated grFETs where the bandgap is tailored with the width: $E_{gap} \sim 1/W$ [eV], W the ribbon width or nanotube diameter in nm. A major and crucial departure from nanotube electronics is that in the grFET semiconducting regions (i.e. narrow ribbons) are seamlessly joined to conducting regions (i.e. wide ribbons) by lithography methods. Hence, in contrast to nanotube and molecular electronics, non-graphitic metallic interconnects are not required. This clearly represents an overwhelmingly important advance over other proposed nano-electronic architectures. In advanced devices the room temperature ballistic properties of nanographite ribbons

will be exploited. Initial investigations will exploit a variety of methods to produce nanoscale graphite objects. Initial prototype devices will be constructed by STM lithography patterning of small graphite samples as demonstrated in this proposal. A critically important engineering challenge is to produce extended epitaxial graphite films on appropriate substrates. Important progress already made in this area (using single crystal SiC wafers) and indicates the path towards large-scale integration of patterned nanographite electronics.

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