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In conclusion, the Equinox 55 Bruker FTIR spectrometer with attached Hyperion Microscope is the core of a network of experimental devices which help us work towards this goal. The principal intended result of our efforts with this apparatus is the development and testing of an JR sensitive focal-plane array of carbon nanotubes. Due to the financial support of AFOSR we now have the critical equipment which will enable us to reach this goal.

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Highly Ordered Carbon Nanotube Arrays and Nanotube–Polymer Nanocomposite Superlattices for Full-Color Sensing and Coating

AFOSR DURIP equipment grant report
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Grant #: F49620-02-1-0242

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Summary

Using the funding from this DURIP program grant, we have acquired an Equinox 55 Bruker Fourier-transform infrared (FTIR) spectrometer to serve as the core research instrument of our carbon nanotube (CNT) infrared research program.

In addition to the FTIR equipment, the grant was able to partially fund the purchase of a Raman microscope and spectrometer setup which provides an invaluable addition to our spectroscopy capabilities for analysis of both CNT samples and other new nanomaterials. The other support for this instrument was provided by Brown University. Finally, funding from this grant was used to acquire an fluorometer to measure the fluorescence emitted from nanotubes and other nanostructures.

This experimental apparatus has been purchased, set up, tested, and integrated with other optical and electronic testing equipment in our labs. In conjunction with a cryostat that was customized to fit into the Bruker spectrometer's observation chamber, we now have the capability of cooling a detector prototype sample to cryogenic temperatures while taking a full spectral survey of its optoelectronic response. In combination with our existing optoelectronic measurement equipment, including a Stanford Research 830 lock-in amplifier and voltage preamplifiers, we can precisely scan narrow IR spectral response windows from 4 K to room temperature. This advanced photoresponse analysis capability leaves us well-poised to be the first lab to build and test a nanotube-based IR optoelectronic device. In turn, this prototype device could form the basis of new sensing and detecting applications.

The experimental setup has been completed and is fully functional as proposed, and is shown in Figure 1.

Although the development of new nanotube-based sensing technologies is the principal purpose of our new experimental installation, the installation also plays a valuable role in other aspects of our research program. We are currently investigating collective radiation processes associated with long-range, coherent interactions between regularly spaced cells in an array of nanopores filled with optically-active materials such as molecules. Similar work is in progress on the optical properties of nanoscale wires and dots engineered using our nanopore fabrication process. The spectrometer will be a valuable tool in studying the optical properties of these new nanoscale systems as well as similar, future systems yet to be conceived and produced using our versatile nanopore fabrication method.

Technical capabilities and objectives

In the area of nanotube science, the principal research field for which our system was acquired, the FTIR system permits accurate and fast characterization of IR absorption, transmission and reflection properties over a broad wavelength range (350–7000 cm^{-1}) and dynamic range (nearly 100% transmission to nearly 100% reflection). These properties are valuable for characterizing a wide variety of CNT samples in different host materials and environments. As a supplement to this, Raman spectroscopy enables investigations of bonding deformation, defects, and changes in the physical properties of nanotubes and molecular composites under different growth conditions, annealing conditions, and electrical or optical excitation.

The primary objectives of our research in this project, which will be the principal, though not the only, beneficiary of this newly acquired equipment, include the following:

- to continue developing our fabrication method to produce, controllably and repeatably, highly-ordered CNT arrays of high-quality and variable dimensions and on various substrates
- to examine and characterize electrical and optical properties of ordered nanotube arrays under IR and UV-Vis excitation
- to explore the device applications of nanotubes in IR detection and UV, visible photosensing and other spectroscopy applications

One goal of this research, and one that has tremendous applications in defense, is the demonstration of highly-ordered CNT arrays and CNT-polymer nano-composites as a new base material for IR detection. Another important goal is the study and development of a new molecular approach to high sensitivity photodetectors and high efficiency solar cells based on novel CNT array-polymer nano-composite superlattices. In addition, there is an important issue associated with the application of CNT array-polymer nano-composites as a material for non-linear optics. It was demonstrated that non-linear optical susceptibility of CNT-polymer composite was below the expected value. We predict that the uniformity and ordering of our CNT arrays will enable the maximum magnitude of the optical non-linearity.

We continue to refine our capability to produce highly-ordered CNT arrays with variable dimensions and increased size of ordered domains. The development of this craft into a reliable technological, and potentially industrial, process requires us to continue our investigations into the formation and self-organization of the aluminum oxide nanochannel templates in which the nanotubes are grown. Additionally, the pyrolytic growth process by which the CNT arrays are formed needs to be examined and optimized in order to facilitate the production of high quality tubes with precisely controlled, variable diameters.

Having begun from a position of leadership in nanotube array fabrication we have already started to study the material properties of these CNT arrays for IR, and UV-Vis detection using our newly acquired and installed experimental apparatus. These ongoing studies will require characterizing the IR spectral characteristics of the CNT arrays and UV-Vis, luminescent properties of CNT-polymer superlattice versus tube diameter and disposition, via broad-area optical measurements (absorption, reflectance and photoconductivity) and locally by means of STM and NSOM spectroscopy on individual nanotubes for a detailed microscopic understanding. These measurements are currently being performed in collaboration with the team of researchers led by Gail Brown (Materials Directorate of the Air Force Research Labs at Wright-Patterson AFB) and also with the Infrared Focal Plane Array Technology Group at JPL. Our new experimental setup has greatly enabled our participation in this collaboration and has facilitated the rapid progress of this project.

The structural properties of the nanotubes are being examined using the high-resolution electron microscopy and scanning probe microscopy facilities available to us at Brown. In anticipation of the IR sensing devices that will be prototyped during the project, we are in the process of developing theoretical models of CNT electron transport taking into account electron-photon scattering within a Green's function formalism, π-π electron interaction between conjugated polymers, and CNTs and electron-phonon scattering rates in quasi-one-dimensional structures.

As the project progresses, having established the optimum conditions and possibilities for high-quality CNT array structure growth we will focus on IR device implementations and engineering of the arrays. In addition to improving the initial prototype detectors, new prototypes will focus on making IR detector arrays on a variety of substrates and in different electrode configurations to determine optimum device parameters. These device explorations will require extensive development of CNT array processing, including surface finishing (wet etching and ion-milling), CNT exposure on both top and bottom, electrode formation (patterned and transparent) and new methods to make reliable contacts to the electrodes without damaging the detectors.

New Results

We have already achieved novel results from a silicon-CNT array heterojunction structure that has been submitted to Physical Review Letters, a most prestigious journal in physics, for publication and has been given favorable reviews and suggestions for revisions. This sample, pictured in Figure 2, displays rectifying behavior depending on the doping level of the silicon as seen in Figure 3. The spectral response of the open-circuit voltage of a CNT/p-type silicon heterojunction is displayed in Figure 4 for various temperatures. The presence of the peak confirms the existence of a space-charge region at the interface between the CNT-array and silicon substrate. The ongoing challenge will be to synthesize samples that exploit CNTs low-bandgap optical and transport properties to push that peak into the IR range. The urgent need for a high level of control in the fabrication process is illustrated in Figure 5, in which we illustrate the significant variation in nanotube properties with diameter.

The equipment acquired through this grant will add to our capabilities for our collaboration with groups at the Air Force Labs at Wright-Patterson AFB and at the Kirtland Base. Our ongoing project has been given significant added potential to open up a broad range of new opportunities for further explorations, some of which have already been identified and are to be pursued in our long term plan.

In conclusion, the Equinox 55 Bruker FTIR spectrometer with attached Hyperion Microscope is the core of a network of experimental devices which help us work towards this goal. The principal intended result of our efforts with this apparatus is the development and testing of an IR sensitive focal-plane array of carbon nanotubes. Due to the financial support of AFOSR, we now have the critical equipment which will enable us to reach this goal.

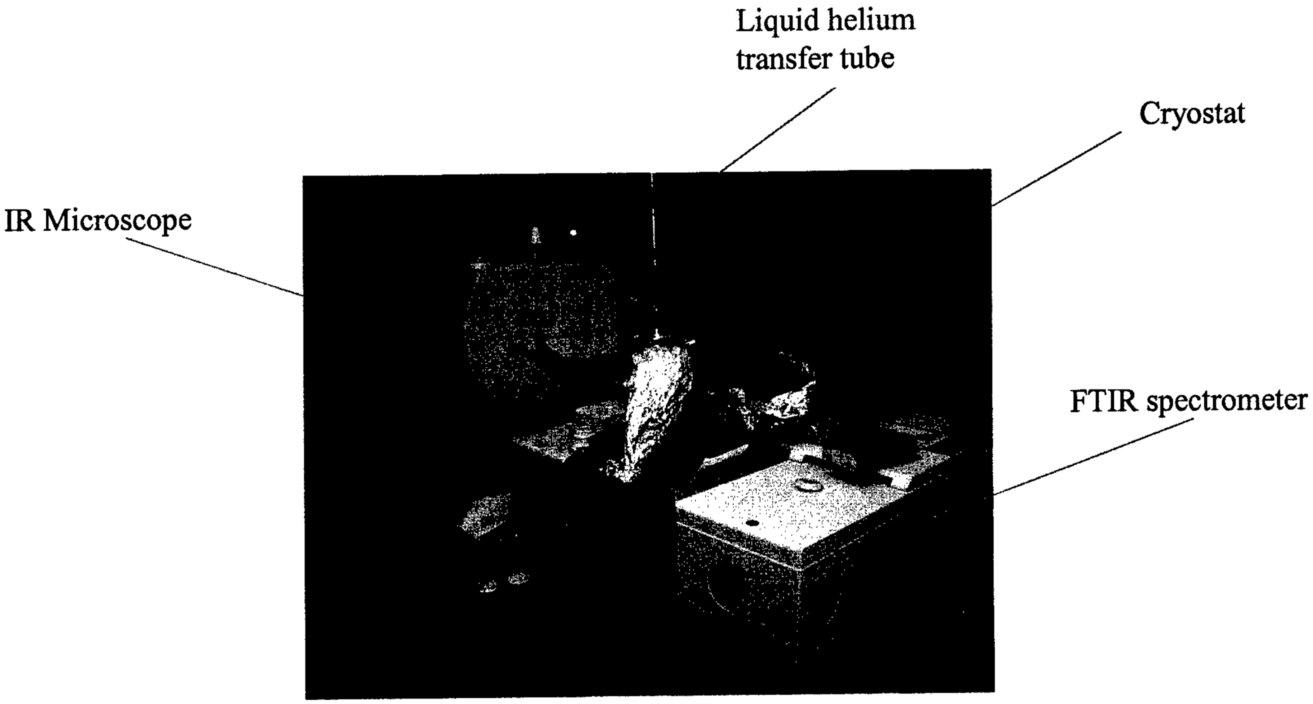

Figure 1. Experimental setup showing FTIR spectrometer, infra-red microscope, and transfer tube for cryogenic operation.

Figure 2. (left) One-pixel prototype of a CNT-based optical detector. (right) Addressable design using crossbar contacts to define detector pixels

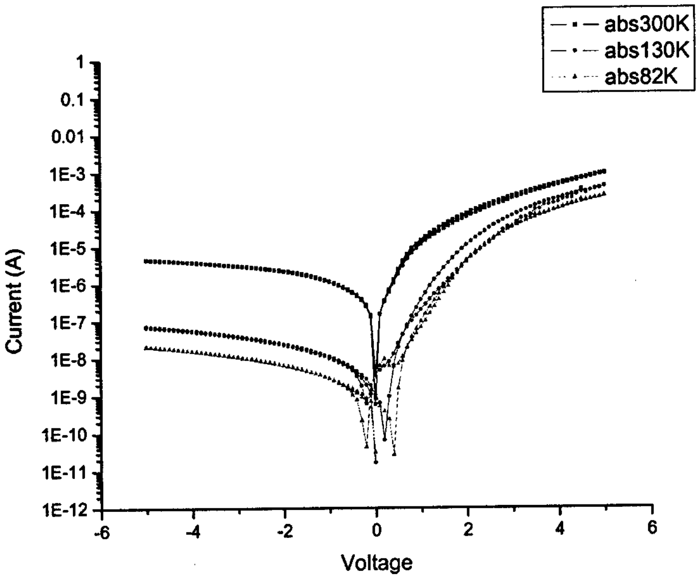

Figure 3. Logarithmic plot of the sample's dark I-V characteristic; rectifying behavior is observed. The forward direction being defined as silicon at ground and the CNTs at positive voltage.

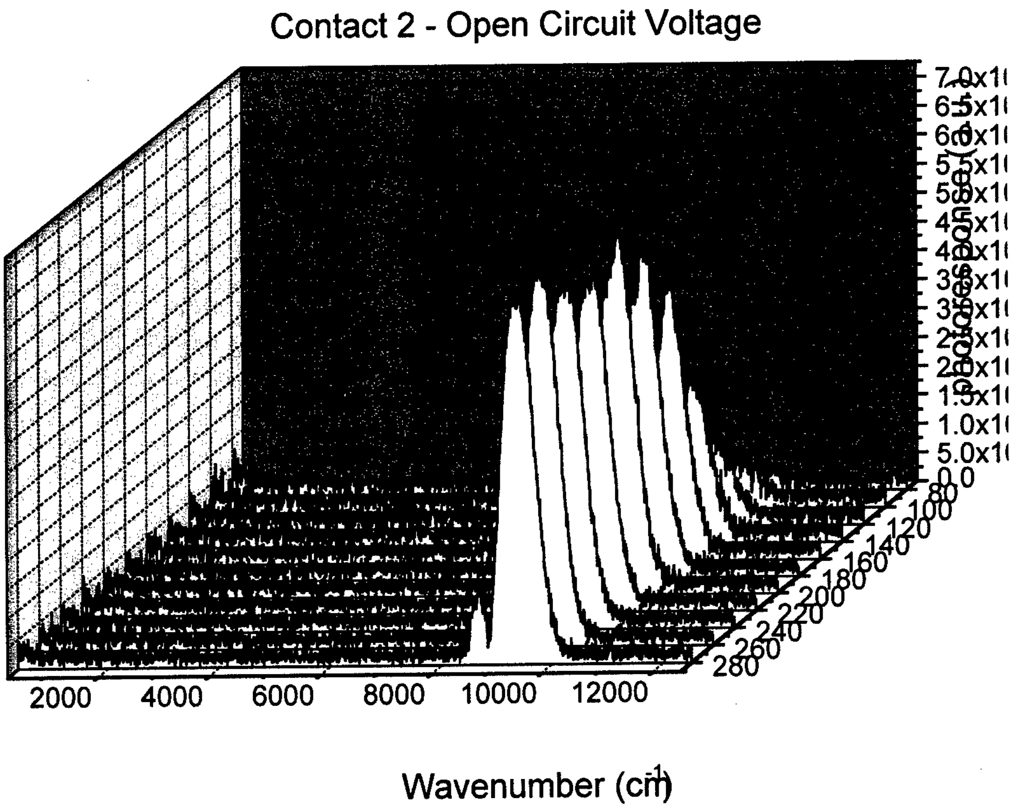

Figure 4. Spectral photovoltage response of CNT-Si heterojunction at different temperatures, showing reduction in photovoltage response as the sample is cooled.

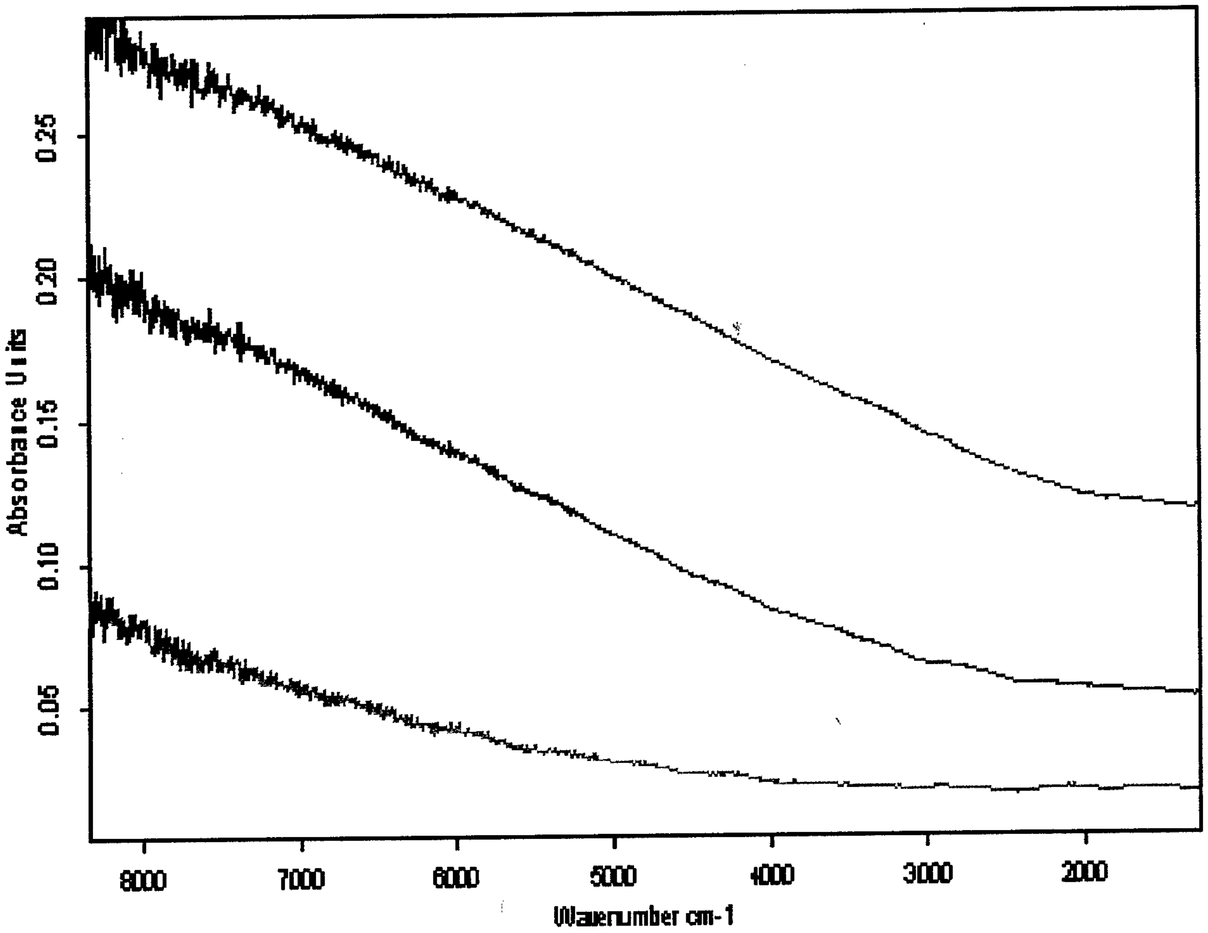

Figure 5. The IR absorbance of uniform nanotubes, freed out of the template, for three different CNT diameters: 75nm—green, 55nm—pink, 35nm—blue. The bandgaps—and corresponding energies—for these three diameters are: E_g (75nm) ~ 246 meV, E_g(55nm) ~ 358 meV, and E_g(35nm) ~ 518 meV.