CENTER FOR APPLIED RADIATION RESEARCH
(CARR)

PRAIRIE VIEW A&M UNIVERSITY

GRANT No. NAG 9-1370

RADIATION EXPOSURE EFFECTS AND SHIELDING ANALYSIS OF CARBON NANOTUBE MATERIALS

FINAL REPORT
JULY 1, 2001 – DECEMBER 31, 2001

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TECHNICAL OFFICER:
LUPITA ARMENDARIZ

August 2002

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1 Background

Carbon nanotube materials promise to be the basis for a variety of emerging technologies with aerospace applications. Potential applications to human space flight include spacecraft shielding, hydrogen storage, structures and fixtures and nano-electronics. Appropriate risk analysis on the properties of nanotube materials is essential for future mission safety. Along with other environmental hazards, materials used in space flight encounter a hostile radiation environment for all mission profiles, from low earth orbit to interplanetary space.

2 Radiation Effects on Carbon Nanotubes

Principal Investigator: R. Wilkins

Staff Engineer: H. Huff

Graduate Student: M. Pulikkathara

Goal: Evaluate the space radiation characteristics of carbon nanotube materials by identifying parametric signatures of radiation damage to the structural and electronic properties of the samples.

NASA Relevance: Carbon nanotube materials promise new strong, lightweight structural materials for spacecraft and may provide means for enhance radiation protection.

Approach: The project represents a Center for Applied Radiation Research (CARR) at Prairie View A&M University collaboration with Rice University and Johnson Space Center. Rice has provided samples and sample characterization. JSC has provided technical support for sample fabrication and characterization. CARR has provided the design and implementation of the radiation experiments, the characterization of the samples before and after irradiation, analyzed and documented experimental data and disseminated the results to the scientific community. Ms. Pulikkathara worked closely with the Rice group, and has been involved in sample fabrication and characterization in the Rice labs. Through this collaboration, Ms. Pulikkathara has learned new characterization techniques and has had access to instrumentation at Rice University.

Experimental: The experiments focused on "bucky papers", which are papers made from single walled nanotubes (SWNT). We have also done some preliminary work on polymer composites with SWNT. We have preformed experiments in three radiation environments relevant to aerospace applications: 40 MeV proton (low earth orbit), 800 MeV protons (cosmic rays) and high-energy neutrons (secondary neutrons in planetary atmospheres, planetary surfaces and spacecraft interiors). Preliminary work on graphite sheets indicated that the electrical resistivity should be a good candidate parameter for studying the radiation effects on the nanotube samples.

CARR research focused on the electrical resistivity of the materials using a standard four-point probe technique. The electrical resistivity is relevant to the electrical and thermal properties of the materials, which will play central roles in aerospace applications. In addition, both CARR and other collaborators studied the material using the technique of Raman spectroscopy.

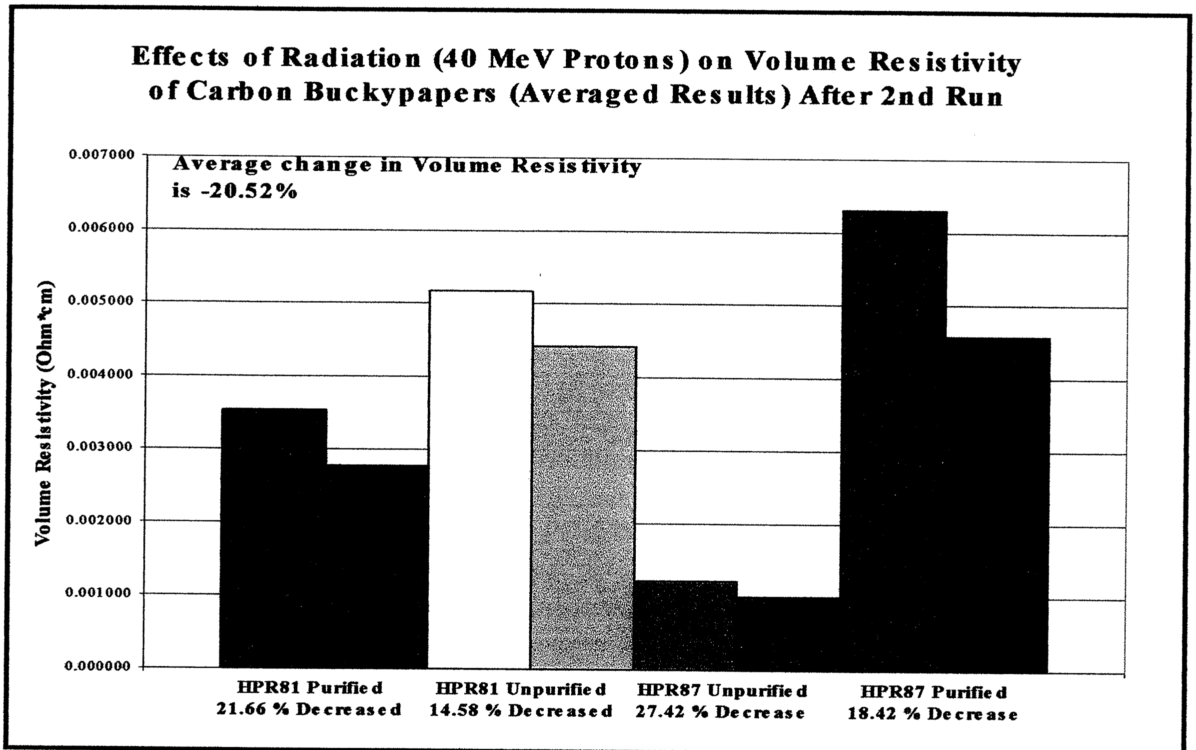

Figure 1: Effects of 40 MeV Proton Radiation on Carbon Buckypapers

Results: Our results indicate the following:

1. The bucky paper samples as compared to graphite controls of similar thickness densities have different responses to each type of radiation.
2. The electrical resistivity of the bucky papers decrease significantly for 40 MeV proton irradiation, tend to increase for 800 MeV protons and show little response to neutron irradiation. An example of the 40 MeV data is given in Figure 1.
3. The character of the changes to the electrical resistivity are consistent from sample to sample under the same radiation environment and do not change with time.

These results suggest that ionization damage may be the predominant damage mechanism for the nanotubes, but the data is still being evaluated. In addition, the Raman data is still under study. The structural information obtained via Raman Spectroscopy along with the electrical information from the resistivity measurements should give clues to the nature of the damage to the nanotubes, plus give information that will allow us to distinguish what role the nanostructure of these materials plays in their radiation characteristics.

Outcomes:

The following presentations and papers have resulted from this project:

1. "Radiation Effects Risk Analysis and Mitigation of Carbon Nanomaterials", R. Wilkins, Lovely K. Fotedar, Alice Lee, Bashir Sayed, Robert Hauge. Presented at the NanoSpace 2001, Galveston, TX, March 2001.[1]
2. "Radiation Effect Risk Analysis and Mitigation of Carbon Nanomaterials and Nanocomposites." M. X. Pulikkathara, R. Wilkins, J. Vera, L. K. Fotedar, E. V. Barrera, T. S. Reese, H. Huff, R. C. Singleterry, B. Syed. Presented by Merlyn Pulikkathara at the Radiation Protection and Shielding Division Topical Proceeding of the American Nuclear Society Conference, Santa Fe, NM, April 2002 (Student author & student presenter).[2]
3. "Energy Dependence of Proton Irradiation Effects on the Electrical Resistivity of Carbon Nanotubes." M. X. Pulikkathara, J. Vera, M. Shofner, R. Wilkins, E. V. Barrera. Presented by Merlyn Pulikkathara at the Nanospace2002 Conference, Galveston, TX, June 2002. (Student author and student presenter).[2]
4. "Proton and Neutron Irradiation Effects on Electrical Resistivity of Single Wall Carbon Nanotubes." M. X. Pulikkathara, J. Vera, M. Shofner, R. Wilkins, E. V. Barrera, J. Read and T. S. Reese. Presented by Merlyn Pulikkathara at the Nanotube2002 Conference, Boston, MA, June 2002. (Student author and student presenter). [2]
5. "Proton and Neutron Irradiation Effects on Electrical Resistivity of Single Wall Carbon Nanotubes." M. X. Pulikkathara, J. Vera, M. Shofner, R. Wilkins, E. V. Barrera, J. Read and T. S. Reese. A poster presentation by Merlyn Pulikkathara at Rice University, August 2002. (Student author and student presenter).
6. "The Center for Applied Radiation Research, Capabilities of Prairie View A&M University in Radiation Research, Experimentation and Modeling", T. Tolpa, R. Wilkins, M. Pulikkathara. Presented at the Houston Nano-Vivo Summit, August 2002. (Student co-author). [2]

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[1] Copy of abstract given in the Appendices.
[2] Copy of paper is given in the Appendices.
[3] Copy of presentation is given in the Appendices.

7. "Fluorinated Single Wall Nanotubes/Polyethylene Composites for Multifunctional Radiation Protection." M.X. Pulikkathara, R. Wilkins, M. Shofner, J. Vera, E.V. Barrera, F. Rodriguez-Macias, R. Viadyanathan, C. Green, C. Condon. To be presented at the 2002 Materials Research Society Fall Meeting in November 2002.

Some other positive experiences resulting from the grant include:

1. Merlyn Pulikkathara, President of the Deans Council, Prairie View A&M University School of Engineering, speaks at the Engineer's Week Awards Ceremony at the university in February 2002.
2. Merlyn Pulikkathara named a NASA Harriet Jenkins Fellow in March 2002.
3. Merlyn Pulikkathara receives award as a Student Speaker at the 12th Biennial RPSD Topical Meeting of the American Nuclear Society in April 2002.[3]
4. Three new funded projects have resulted from the initial collaboration.

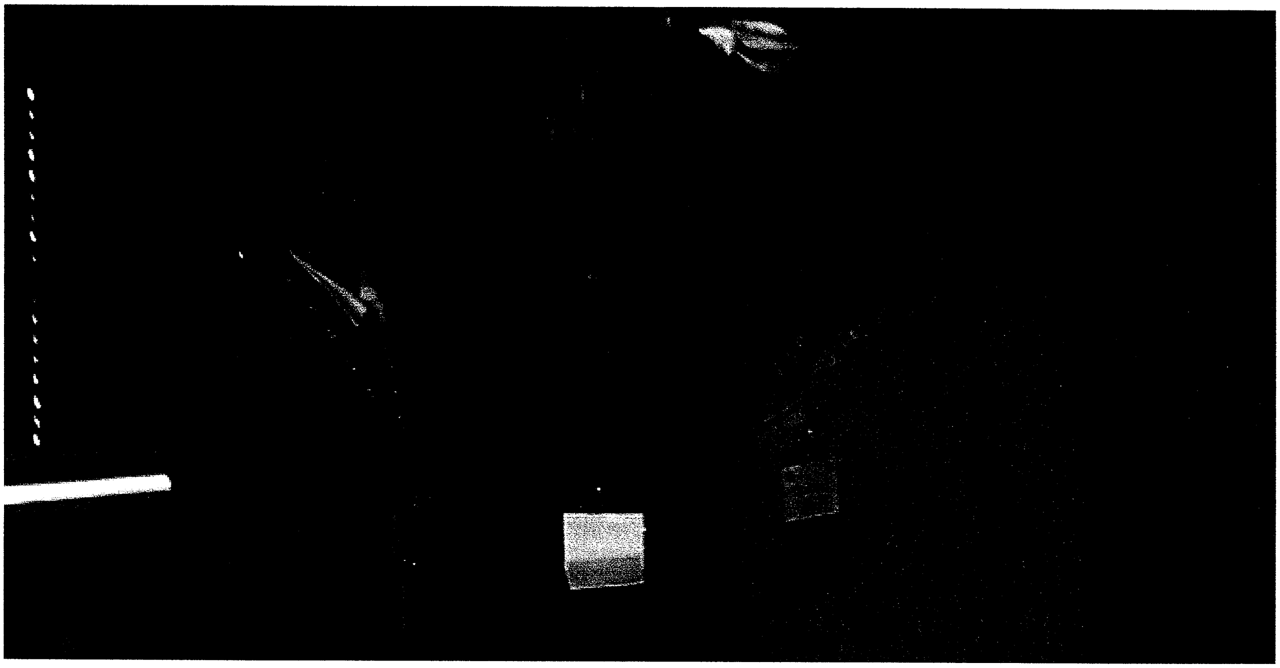

Photo 1: Dr. Bonnie Dunbar, Merlyn Pulikkathara & Harriet Jenkins at the NASA Harriet Jenkins Fellowship Award Ceremony, March 2002.

[4] Copy of award given in the Appendices.

3 APPENDICES

3.1 Nanospace2001, Galveston, TX, March 2001. Abstract & Presentation - "Radiation Effects Risk Analysis and Mitigation of Carbon Nanomaterials", R. Wilkins, Lovely K. Fotedar, Alice Lee, Bashir Sayed, Robert Hauge.

NANOSPACE 2001

Exploring Interdisciplinary Frontiers

The International Conference on
Integrated Nano/Microtechnology for Space and
Biomedical Applications

March 13-16, 2001

National Aeronautics and Space Administration (NASA)

Host:
The Institute for Advanced Interdisciplinary Research (IAIR)

Conference Location:
Moody Gardens Hotel on historical Galveston Island
just a short drive south of Houston on the Texas Gulf Coast

Session 2c

NanoMaterials Safety and Measurement (I)

Session Co-Chairs – Dr. Rafat Ansari, NASA Glenn Research Center
Jon Read, NASA Johnson Space Center, Science Applications International Corporation

1:00 PM "Surface adhesion studies of nanoscale materials with laser-generated surface accoustic waves." S. N. Zherebtsov, A. A. Kolomenski, and H. A. Schuessler, Department of Physics, Texas A&M University.

1:30 PM "Automated Size and Shape Analysis of Micrometer Size Particles Using Digital Image Analysis and Potential for Nanometer Size Range." Dayakar Penumadu, Center for Advanced Materials Processing, Clarkson University.

2:00 PM "Non-invasive Characterization of Nano Particles in Solutions." Rafat Ansari, NASA Glenn Research Center.

2:30 PM "Radiation Effects Risk Analysis and Mitigation of Carbon Nanomaterials." Richard Wilkins, Lovely K. Foredar, Alice Lee, Bashir Syed, Robert Hauge, NASA Center for Applied Radiation Research, Prairie View A&M University, Science Applications International Corporation, NASA Johnson Space Center, Rice University.

RADIATION EFFECTS RISK ANALYSIS AND MITIGATION OF CARBON NANOMATERIALS

Richard Wilkins[1], Lovely K. Fotedar[2], Alice Lee[3], Bashir Syed[2], Robert Hauge[4], Enrique Barrera[4] and Gautam D. Badhwar[3]

[1]NASA Center for Applied Radiation Research, Prairie View A&M University, Prairie View, Texas 77446
[2]Science Applications International Corporation, NASA Johnson Space Center - Code NX, Houston, Texas 77058
[3]NASA-Johnson Space Center, Safety, Reliability, and Quality Assurance, Houston, Texas 77058
[4]Center for Nanoscale Research and Technology, Rice University, Houston, Texas
[5]Materials Testing Laboratory, Rice University, Houston, Texas

We describe a new program to analyze risk of space radiation damage effects on carbon nanomaterials. Ground test protocols will assess radiation degradation (or possibly enhancement) of electronic and mechanical properties of carbon nanomaterials. Mitigation properties of these materials will be studied by measuring the effects of intervening materials on changes in single event upset rates on 4MB SRAM and changes in the linear energy transfer spectrum, dose and dose rate as measured by a tissue equivalent proportional counter (TEPC). The ground tests will be conducted with a variety of radiation test beams to study both ionizing radiation effects and radiation induced displacement damage.

We have conducted some baseline experiments using thin (0.254mm) graphite foils irradiated with a broad spectrum high-energy (1-800 MeV) neutron beam at the Los Alamos Neutron Science Center (LANSCE). This beam simulates the secondary neutron spectra in the atmosphere and closely resembles the expected secondary neutron spectra on the International Space Station. The LET spectrum, total dose and dose rate as monitored by a TEPC are compared with no intervening foil (the foil is upstream from the TEPC in the beam) and with the foil. It is observed that the foil substantially affects the LET spectrum and increases the tissue equivalent dose rate by a factor greater than 3.5. Based on this data, measurable effects should be detectable with the current instrumentation for nanotube shielding paper as thin as 10 microns.

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RADIATION EFFECTS RISK ANALYSIS
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Richard Wilkins[1], Lovely K. Fotedar[2], Alice Lee[3],
Bashir Syed[2], Robert Hauge[4], Enrique Barrera[5] and Gautam D. Badhwar[3]

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[2]Science Applications International Corporation, NASA Johnson Space Center - Code NX, Houston, Texas 77058
[3]NASA-Johnson Space Center, Safety, Reliability, and Quality Assurance (Code NX) and Space and Life Sciences (Code SN), Houston, Texas 77058
[4]Center for Nanoscale Research and Technology, Rice University, Houston, Texas
[5]Materials Testing Laboratory, Rice University, Houston, Texas

NanoSpace 2001

March 13, 2001

Prairie View A&M University
Center for Applied Radiation Research (CARR)

Motivation

- Nanotube materials have a number of space applications:
  - Spacecraft structures,
  - Radiation protection applications,
  - Nanoelectronics,
  - Etc.
- Questions for radiation risk and mitigation assessment:
  - How tolerant are these novel materials to space radiation?
  - What are the radiation transport characteristics of these materials?
  - What are the best methods for accessing these properties?
- Need: <u>Develop a radiation test protocol.</u>
- Problem: Paucity of Nanotube Samples
- Solution: <u>Baseline measurements on thin graphite sheet.</u>

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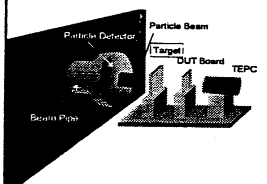
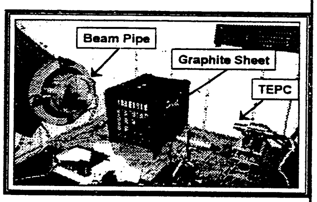
Los Alamos Neutron Beam Test Setup





TEPC = Tissue Equivalent Proportional Counter.
- Measure Radiation Dose Equivalent Rates
- Changes In The Lineal Energy Spectra

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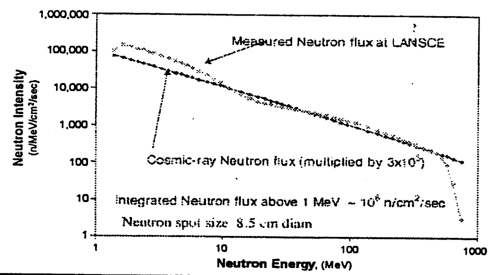
Neutron Flux at 30° L Flight Path



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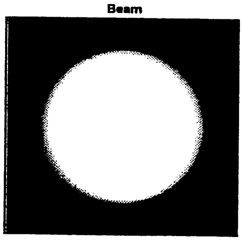
Neutron Radiographs

Beam



TEPC in the beam

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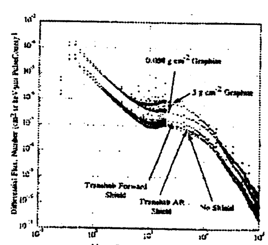
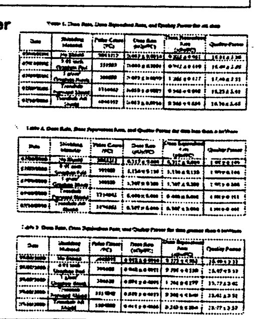
Tissue Equivalent Proportional Counter (TEPC) Data





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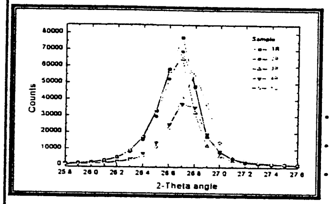
X-Ray Defractometer Data



Sampie	002 peak 2-Theta (degree)	Counts
1R	26.7	77390
2R	26.7	68962
3R	26.7	64534
4R	26.7	37146
5U	26.8	55540

- Irradiated Peak Larger ⇨ Higher Crystallinity
- Consistent with Resistivity Data
- Peak Shift for Irradiated vs. Non-Irradiated?

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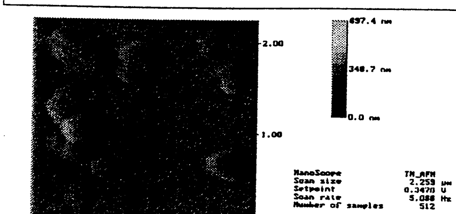
Atomic Force Microscope (AFM) Image



Dimple Height ~ 175 nm

Irradiated Sample: 7R

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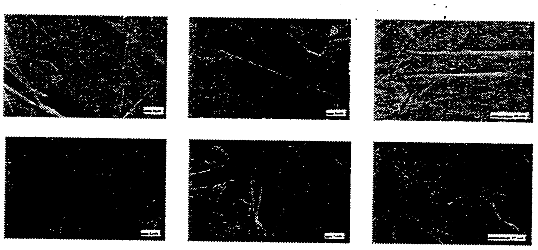
Scanning Electron Microscope (SEM) Micrographs



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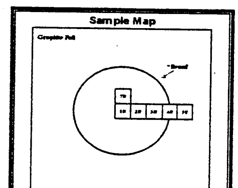
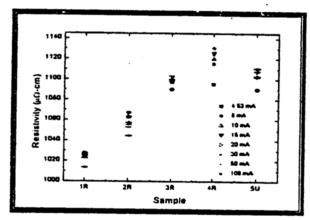
Four Point Probe Resistivity Measurement





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Acknowledgments

- Experimental Work:
  - Neutron Irradiation: H. Huff
  - Resisting Measurements: M. Marrero, S. Wilson*, R. Dwivedi
  - Atomic Force Microscopy: M. Marrero, M. Pulikkathara*
  - X-Ray Diffractomter: S. Lin
  - Scanning Electron Microscopy: M. Marrero
  - * Undergraduate Student Researchers.
- Viewgraphs: S. Ardalan
- Support: National Aeronautics and Space Administration

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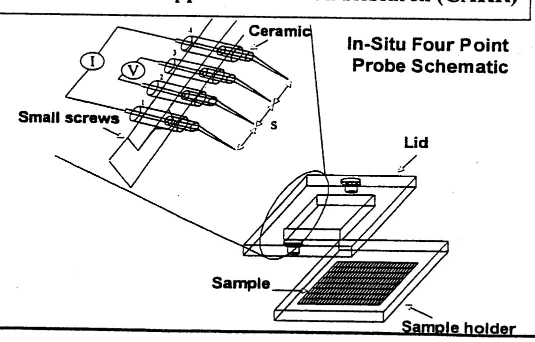
In-Situ Four Point Probe Schematic



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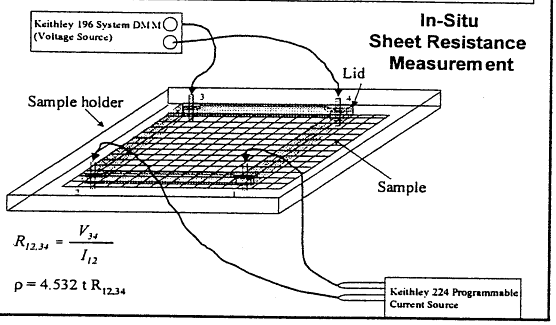
In-Situ Sheet Resistance Measurement



$$R_{12,34} = \frac{V_{34}}{I_{12}}$$

$$\rho = 4.532\ t\ R_{12,34}$$

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Summary

- We have explored methods of gauging radiation damage on thin graphite sheets to help determine a radiation test protocol for nanotube materials.
- The TEPC observed a substantial effect due to thin (0.254mm) graphite foil.
  - Expect 10um nanotube material to have a measurable effect.
- Sheet resistivity data suggests that it is a candidate for in-situ damage studies.
- X-Ray Diffraction data indicates an increase in crystallinity with radiation in graphite.
- It is not clear if AFM and SEM will be useful in gauging radiation damage.

3.2 ANS 2002 Paper & Presentation Notes - "Radiation Effect Risk Analysis and Mitigation of Carbon Nanomaterials and Nanocomposites." M. X. Pulikkathara, R. Wilkins, J. Vera, L. K. Fotedar, E. V. Barrera, T. S. Reese, H. Huff, R. C. Singleterry, B. Syed. Presented by Merlyn Pulikkathara at the Radiation Protection and Shielding Division Topical Proceeding of the American Nuclear Society Conference, Santa Fe, NM, April 2002 (Student author & student presenter).

RADIATION EFFECT RISK ANALYSIS AND MITIGATION OF CARBON NANOMATERIALS AND NANOCOMPOSITES

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SUMMARY

Carbon nanotube samples were irradiated with 40MeV protons, simulating low earth orbit (LEO) levels of space radiation exposure. Samples were then characterized using four-point probe bulk resistivity and Raman spectroscopy. The resistivity measurements revealed a decrease in bulk resistivity post-radiation exposure. An average decrease of about 20% was observed applying ambient air and temperature conditions. Raman results are inconclusively; however, interpretation of the preliminary Raman results is continuing in comparison with other radiation test results.

I. BACKGROUND

Space exploration has been and will continue to be increasingly dangerous to our astronauts and related electronics as we venture further into space. The space environment has three sources of radiation: Galactic Cosmic Rays (GCR), solar energetic particles, and particles within the geomagnetic field.[1] The risk of radiation exposure during a long duration mission limits the total dose allowed for astronauts during their lifetime. If more effective radiation shielding can be developed, the personnel and electronics would be able to withstand the hazardous space environment for a longer period of time without increased risk. Many materials have been investigated[2], and research for a cost-effective material that would reduce the effects of energetic protons from GCR is continuing.

Desired materials would need to be lightweight, to keep the transport of such material cost effective on long missions. In addition, materials with a high hydrogen density are preferred, because the use of hydrogen materials also reduces the spallation fragments associated with higher Z atoms. These fragments can increase radiation damage to personnel and electronics. Materials with structural properties that are radiation resistant are also needed for future spacecraft.

Carbon nanotubes have been explored for a variety of applications.[3] For example, their provocative geometry (Figure1) suggests that they could be used to form hydrogen filled composites that could be used for both space craft structure, radiation shielding and fuel storage. The properties of Single Wall Nanotubes (SWNT) and related materials have been studied for their hydrogen absorption capacities, as a strengthener in composites and other potential aerospace application. However, little work has been done to investigate the tolerance of these materials to radiation environments relevant to aerospace missions.

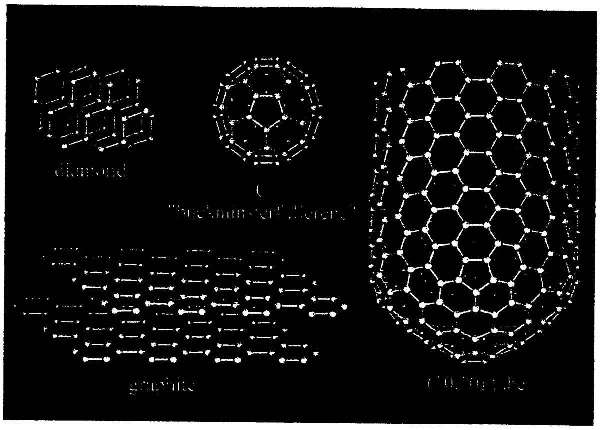

Figure 1. Different structural forms of carbon are shown here (from www.cnst.rice.edu/pics.html)

In this paper, we describe results from part of an ongoing study to determine the radiation characteristics of SWNT related materials. We are exploring methods to quantify radiation effects on the materials and elucidate the damage mechanisms for these nanoscale-structured materials. For the "bucky paper" samples, we have observed a consistent resistivity change correlated with radiation. Raman spectroscopy results have been less straightforward and interpretation of the Raman data continues.

II. EXPERIMENTAL

The SWNT were fabricated using the High Pressure Carbon Monoxide (HiPCO) [4] process. The SWNTs were dissolved in isopropanol and then filtered to make the buckypapers. Each paper averaged a diameter of 4cm and varied in thickness according to time spent on the filter. A typical thickness ranged from about 60 to 400 um. There were 14 buckypapers from a batch referred to as "HiPCO HP 81" that contained iron catalyst, but 7 of those papers were purified to remove the iron content. The papers were then divided into two stacks of raw (unpurified) and pure materials and each stack was placed between two sheets of Mylar for stability (Figure 2). A second batch (HiPCO HP-87) of 15 papers was made with an iron-nickel catalyst, and was similarly divided into two stacks of eight raw and seven purified of the nickel catalyst. These samples were similarly packaged with Mylar for radiation testing.

Data reported below comes from two separate radiation runs with 40 MeV protons at the Texas A&M Cyclotron Institute[5]. Protons of this energy are typical of those encountered in low earth orbit (LEO). Typical flux rate was approximately 1 X 10^7 p/cm^2/s. Samples were irradiated to a fluence of 3X 10^{10} p/cm^2 for each run. Figure 3 illustrates one of the buckypaper samples in the radiation chamber at the Texas A&M Cyclotron.

On the first run, only samples of HP-81 were radiated. Due to sample availability constraints, 6 out of 7 HP-81 raw buckypapers and all 7 of HP-81 "pure" buckypapers were tested by four point probe only after irradiation. In addition, all samples were also characterized by Raman after irradiation. Note that only one HP-81 raw sample had pre- irradiation resistivity measurements taken. These samples were then re-irradiated during a second 40 MeV beam run along with HP-87 samples. Of the HP-87 samples irradiated during the second experiment, a complete set of pre- and post-irradiation data for four- point probe and Raman was obtained. Table 2 lists the samples used for each radiation run.

Table 1: Buckypapers used for this study

40 MeV Beam Date	Buckypaper radiated	Catalyst
06/09/01	HP81 raw (single1)	Fe
06/09/01	HP81 raw (stack of 6)	Fe
06/09/01	HP 81 pure (stack of 7)	Fe
07/21/02	HP81 raw (stack of 6)	Fe
07/21/02	HP 81 pure (stack of 7)	Fe
07/21/02	HP87 raw (stack of 6)	Ni
07/21/02	HP 87 pure (stack of 7)	Ni

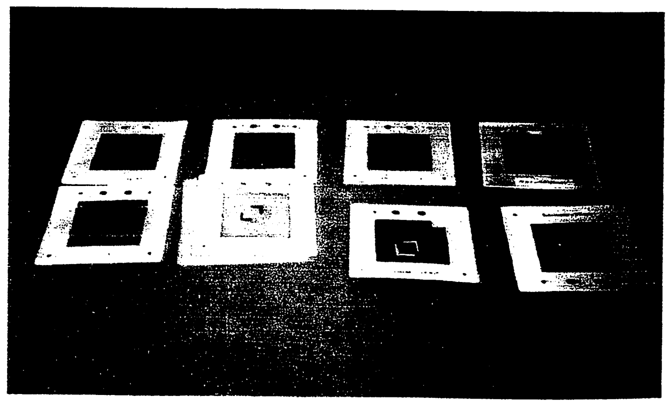

Figure 2. The two right samples in the top row are HP-81 raw and purified samples; they were placed between two Mylar sheets and held in frames to fit into the radiation chamber.

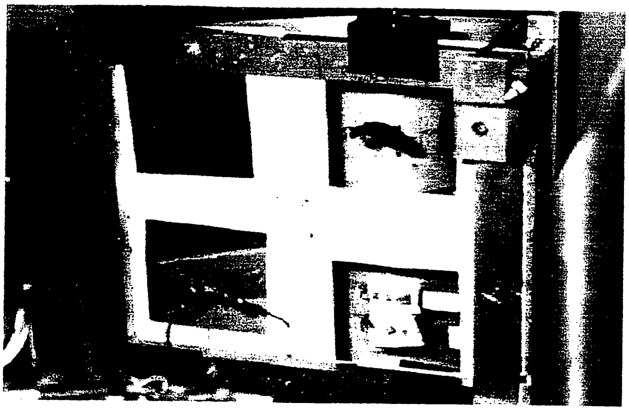

Figure3. One of the buckypapers samples in Figure 2 (top left) is shown in position within the radiation test chamber at the Texas A&M Cyclotron.

Resistivity measurements were taken with a standard four- point probe apparatus using a programmable current source and a digital multimeter. Current values were manually selected from 1 to 50 milli -amps and the voltage was read from the multimmeter. A total of over 1400 measurements were taken in ambient air and temperature. Resistivity was then calculated using the appropriate formula for the probe head configuration and sample thickness. The Raman measurements focused on a breathing mode peak and a "tube peak" that is characteristic of single walled nanotubes. It was hoped that significant shifts in these peaks would indicate radiation induced displacement damage.

III. RESULTS AND DISCUSSION

Table 2 summarizes the observed changes in bulk resistivity for the samples used in these experiments. The overall average change in resistivity is a 20.52% decrease. This excludes the one HP-81 Raw sample in which only a 4% decrease was observed after $3X10^{10}$p/cm^2 irradiation.

Table 2. Total fluence and resistivity changes for the buckypaper samples

Buckypaper Name	#of papers	Fluence p/cm^2	$\Delta\rho_{bulk}$ (%change)
HP 81Raw	1	$3X10^{10}$	-4%
HP 81Raw	6	$3X10^{10}$	*
HP 81 Pure	7	$3X10^{10}$	*
HP 81 Raw	6	$6X10^{10}$	-14.58%
HP 81 Pure	7	$6X10^{10}$	-21.66%
HP 87 Raw	7	$3X10^{10}$	-27.42%
HP 87 Pure	8	$3X10^{10}$	-18.42%

* = No pre-irradiation information available

From the data, there does not appear any correlation between the percent-change in resistivity with either total fluence, catalyst used for fabrication, or purity of material. However, an overall decrease is observed for all samples.

This result is consistent with previous result on graphite irradiated with high-energy neutrons [6]. In that experiment, pure graphite sheets were irradiated to a fluence of about $1x10^{10}$ n/cm^2 with a broad-spectrum neutron beam with energies from 1 to 800 MeV at the Los Alamos Neutron Science Center. It was observed that a small decrease in the graphite's resistivity of 4.5% correlated with an increase in the overall crystallinity in the material as measured by X-ray diffraction. It is believed that this phenomenon is due to the well-known process of embrittlement. In this process, the energy deposited by irradiation enhances atomic diffusion and re-crystallization.

However, given the structural difference between the buckypapers and graphite at the microscopic level (Figure 1), it may be that a different mechanism is responsible for the observed changes in the buckypapers. We speculate that structural changes in the nanotubes that makeup the buckypaper may be responsible for the change in overall resistivity of the nanotubes that make up the buckypapers. To date, we have not been able to perform diffraction experiments on the irradiated buckypaper samples in the attempt to quantify changes in atomic order. We are currently exploring diffraction methods to elucidate our results.

Raman results suggest some structural change, but these studies are inconclusive and continuing.

ACKNOWLEDGEMENTS
Funding for this project came from NASA, partly through the Center for Applied Radiation Research at Prairie View A&M University (Grant Nos. NCC 9-114 and NAG 9-1370).

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5. http://cyclotron.tamu.edu
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RADIATION EFFECT RISK ANALYSIS AND MITIGATION OF CARBON NANOMATERIALS AND NANOCOMPOSITES

M.X. Pulikkathara[1], R. Wilkins[1]
Jerry Vera[2], Lovely K. Fotedar[3], E. V. Barrera[2], Thomas S. Reese[4], Harold Huff[1], Robert C. Singleterry[5], Bashir A. Syed[3]
[1]Center for Applied Radiation Research
Prairie View A&M University
[2]Rice University
[3]Science Applications International Corporation
[4]NASA Langley Research Center
[5]Washington Group International

Funding for this project was possible through NASA Grant # NCC9-144 and NAG 9-1370 through the
Johnson Space Center

Outline

- Why study radiation in space?
- Parameters for effective radiation shielding materials.
- Carbon nanomaterials.
- Experiment: Four Point Probe Method
- Results
- Discussion
- Acknowledgements

Why study space radiation?

- Space environment has three sources of radiation: galactic cosmic rays, solar energetic particles, and particles within the geomagnetic field.
- The risk of radiation exposure increases with long term missions and limits the total dose allowed for astronauts during their lifetimes. Effective radiation shielding must be used for the protection of the astronauts and associated electronics.

Why study new materials for radiation shielding ?

- The need for materials with enhanced radiation protection properties
- The need for cost effective materials
- The need to reduce weight (The cost is about $10,000/lb for flight into space.)

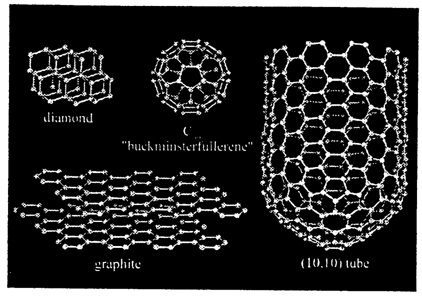
Parameters for effective radiation shielding materials

- Materials with low Z atoms reduce fragmentation and are lighter weight
- Materials with higher hydrogen density tend to have better shielding characteristics
- Materials should be radiation resistant to maintain structural integrity

Why study Single Wall Nanotubes(SWNT) ?

- Nanotubes are strong and lightweight
- Provocative geometery suggest a means for hydrogen storage (results to date are controversial)
- SWNT are easily incorporated into hydrogen rich polymer composites
- Prelimary data suggests that SWNT/Polyethylene composites are structurally radiation resistant (For future talk)

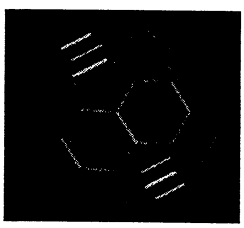
Forms of Carbon



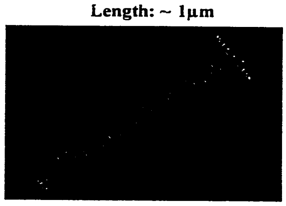
From Cnst.rice.edu/pics.html.

Bucky ball and nanotube

Diameter: 1nm



Diameter: ~1nm
Length: ~ 1μm

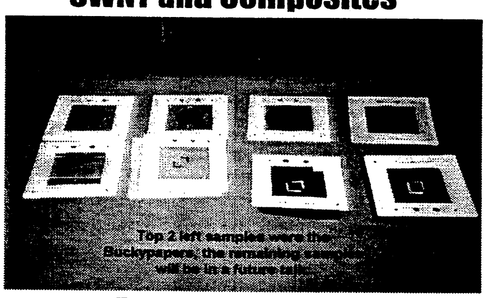


Cnst.rice.edu/pics.html

40 Mev Proton Irradiations

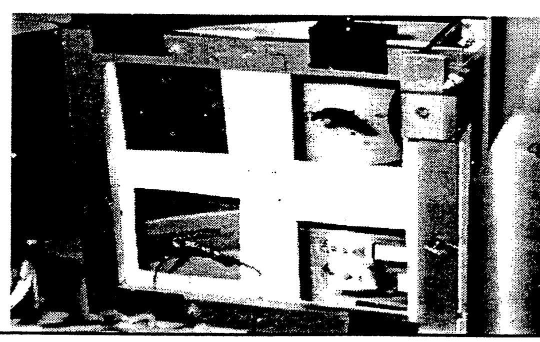
- Two runs at the Texas A&M Univeristy Cyclotron Institute:
  - 1. An initial batch of "81" SWNT Buckypapers,(raw and purified materials)
  - 2. The same "81" samples and a new batch "87" SWNT Buckypapers (raw and pure materials)
- This energy is relevant to low earth orbit.

SWNT and Composites

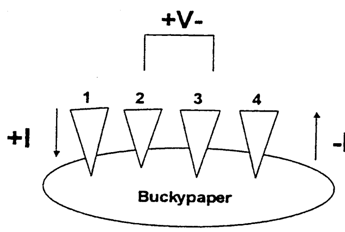


Texas A&M University Cyclotron

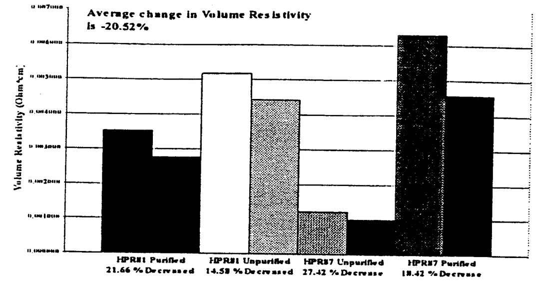
Samples in Texas A&M Cyclotron Institute



Resistivity Measurements Schematic of Four Point Probe

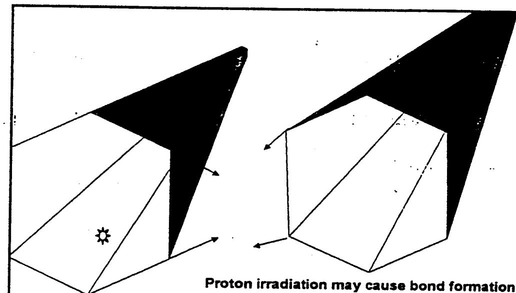


Effects of Radiation (40 MeV Protons) on Volume Resistivity of Carbon Buckypapers (Averaged Results) AFTER 2nd Run



Data Results of Four point probe

Buckypaper Name	#of papers	Fluence p/cm^2	$\Delta\rho_{bulk}$ (%change)
HP 81Raw	1	$3X10^{10}$	-4%
HP 81Raw	6	$3X10^{10}$	*
HP 81 Pure	7	$3X10^{10}$	*
HP 81 Raw	6	$6X10^{10}$	-14.58%
HP 81 Pure	7	$6X10^{10}$	-21.66%
HP 87 Raw	7	$3X10^{10}$	-27.42%
HP 87 Pure	8	$3X10^{10}$	-18.42%



Proton irradiation may cause bond formation between nanotubes, resulting in a greater network of conductive SWNT to account for the drop in resistivity. It is possible that this bond formation may account for why the single "81" Buckypaper had less of a resistivity decrease compared to the stacks of Buckypaper, in which the nanotubes may have connected between layers of the Buckypapers.

Where are we now?

- Measurements indicates an average of 20% decrease in resistivity.
- Four point probe technique as well as RAMAN spectroscopy have been done on all 40MeV proton samples.
- Data analyses for (Raman) continuing, working on X-ray diffraction.
- Research project is in progress.

Nano Group PVAMU & RICE from Summer 2001 at Los Alamos National Laboratory

800MeV proton irradiation (Future talk)

Thank you !!!

Noah Rattler, undergraduate researcher CARR PVAMU

- Dr. Richard Smalley, assisting in the establishing of our collaboration
- Texas A&M Cycletron personnel
- Los Alamos National Laboratory personnel
- American Nuclear Society

Questions/Suggestions?

3.3 Nanospace2002 Presentation - "Energy Dependence of Proton Irradiation Effects on the Electrical Resistivity of Carbon Nanotubes." M. X. Pulikkathara, J. Vera, M. Shofner, R. Wilkins, E. V. Barrera. Presented by Merlyn Pulikkathara at the Nanospace2002 Conference, Galveston, TX, June 2002. (Student author and student presenter)

Energy Dependence of Proton Irradiation Effects on the Electrical Resistivity of Carbon Nanotube Papers

M.X. Pulikkathara[1]
Meisha Shofner [2], Jerry Vera[2],
R. Wilkins[1], E. V. Barrera[2],
[1]Center for Applied Radiation Research
Prairie View A&M University
[2] Department of Mechanical Engineering and Material Science
Rice University

Funding for this project was possible through NASA Grant # NCC9-144 and NAG 9-1370 through the **Johnson Space Center**

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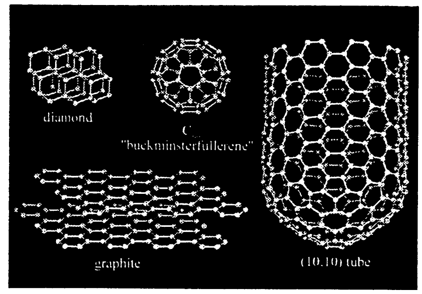
Forms of Carbon



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- This energy is relevant to low earth orbit missions.
- Two runs at the Texas A&M Univeristy Cyclotron Institute:
  - 1. An initial batch of "81" SWNT Buckypapers,(raw and purified materials)
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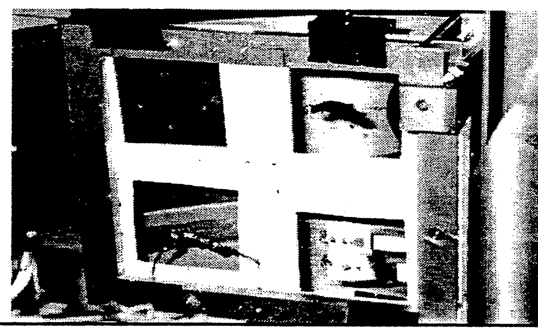
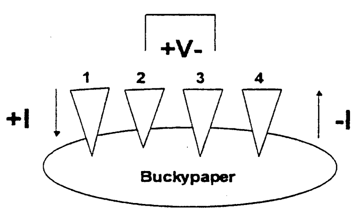
Samples in Texas A&M Cyclotron Institute

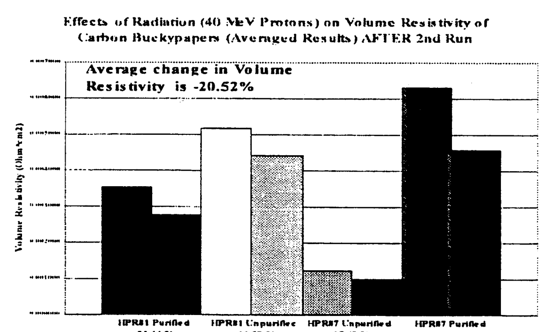


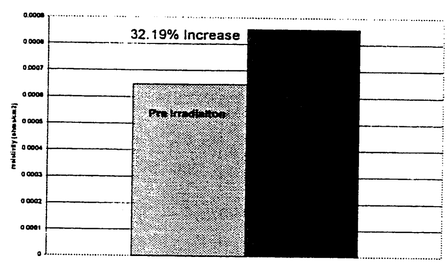
Resistivity Measurements Schematic of Four Point Probe



ρ^{*}_{bulk} = Voltage/Current *8.532 *thickness of buckypaper

*Measurements were taken in ambient temperature





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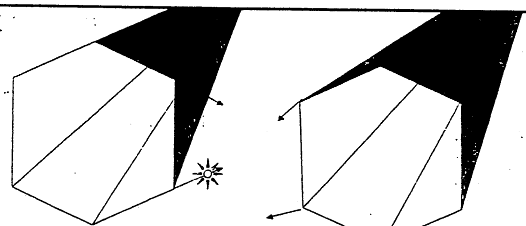


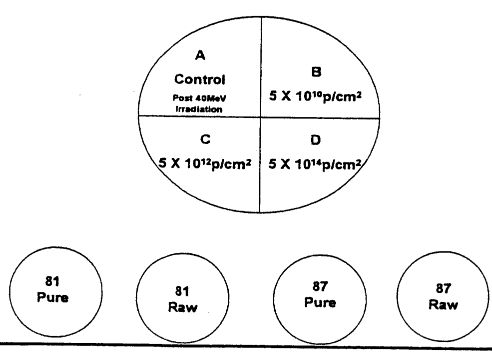
•Proton irradiation may cause bond formation between nanotubes, resulting in a greater network of conductive SWNT to account for the drop in resistivity.

•It is possible that this bond formation may account for why the single "81" Buckypaper had less of a resistivity decrease compared to the stacks of Buckypaper, in which the nanotubes may have connected between layers of the Buckypapers.

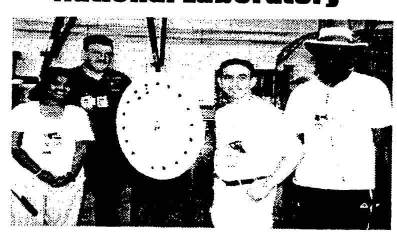
Experiment 2: 800MeV Proton Irradiations

- 800 MeV protons are representative of protons that constitute the cosmic ray spectrum which is significant to exploration class missions.
- The nanopapers (raw and purified) that were irradiated with 40 MeV protons from Experiment 1and grafoil (comparison) papers were quartered into control, 5X10^{10} protons/cm^2, 5X10^{12}protons/cm^2, and 5X10^{14} protons/cm^2

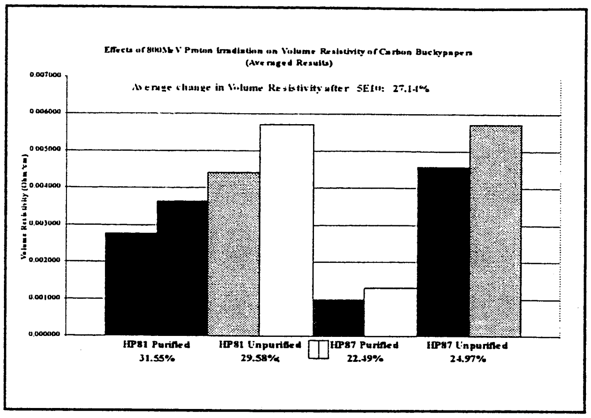
Diagram of Quartered Nanopapers

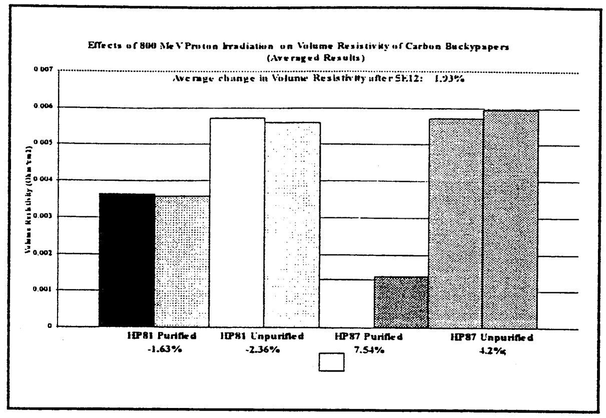


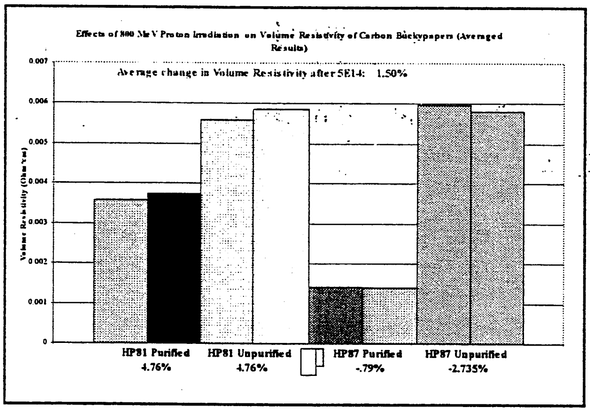
Nano Group PVAMU & RICE from Summer 2001 at Los Alamos National Laboratory

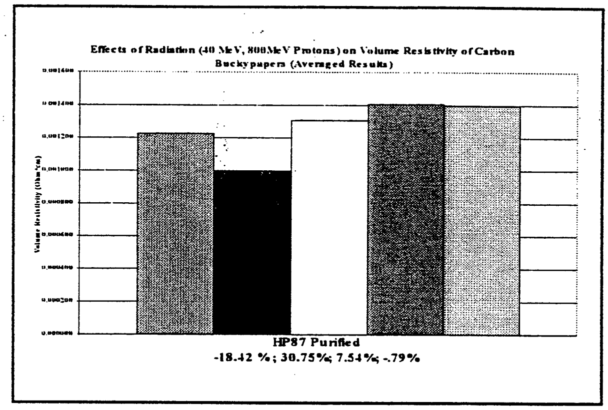


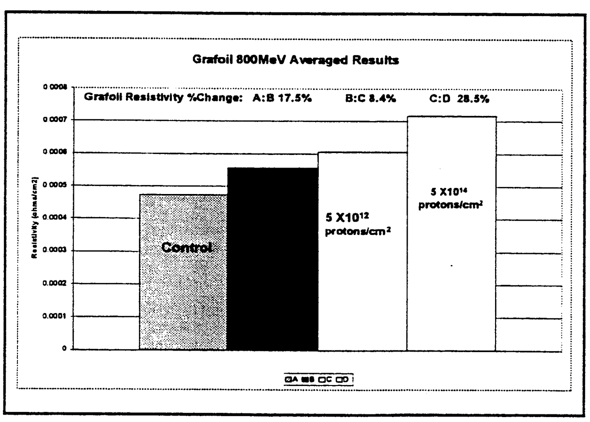
800MeV proton irradiation











Summary of Results

- **40Mev**
  - Bucky papers had -20% decrease in bulk resistivity.
  - Grafoil papers had a 32% increase in bulk resistivity.
- **800 MeV**
  - Bucky papers had an increase 29.15%, 1.9%, and 1.5% in resistivity after fluences of $5X10^{10}$, $5E10^{12}$, & $5X10^{14}$ protons/cm^2 respectively.
  - Grafoil increased by 17.4%, 8.4% & 28.5% in resistivity after similair fluences.

Where are we now?

- Raman spectroscopy of samples in progress.
- Neutron irradiation to be presented for future talk.
- In search of theorist /modeler interested in radiation effects of carbon materials for collaboration.

Thank you !!!

- Noah Rattler, undergraduate researcher CARR PVAMU
- Dr. Richard Smalley, assisting in the establishing of our collaboration
- Texas A&M Cyclotron personnel
- Los Alamos National Laboratory personnel
- IAIR, Nanospace2002

Questions/Suggestions?

3.4 Nanotube 2002 Presentation - "Proton and Neutron Irradiation Effects on Electrical Resistivity of Single Wall Carbon Nanotubes." M. X. Pulikkathara, J. Vera, M. Shofner, R. Wilkins, E. V. Barrera, J. Read and T. S. Reese. Presented by Merlyn Pulikkathara at the Nanotube2002 Conference, Boston, MA, June 2002. (Student author and student presenter).

Proton and Neutron Irradiation Effects on the Electrical Resistivity of Single-Walled Carbon Nanotubes

M.X. Pulikkathara[1]
Meisha Shofner [2], Jerry Vera[2],
R. Wilkins[1], E. V. Barrera[2], Jon Read[3], Thomas S. Reese[4]
[1]Center for Applied Radiation Research
Prairie View A&M University
[2] Department of Mechanical Engineering and Material Science
Rice University
[3] NASA Johnson Space Center
[4] Washington Group International

Motivation

- Space environment has three sources of radiation: galactic cosmic rays, solar energetic particles, and particles within the geomagnetic field.
- The risk of radiation exposure increases with long term missions and limits the total dose allowed for astronauts during their lifetimes. Effective radiation shielding must be used for the protection of the astronauts and associated electronics.
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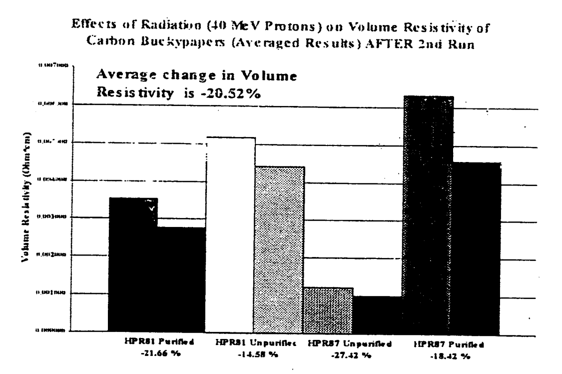
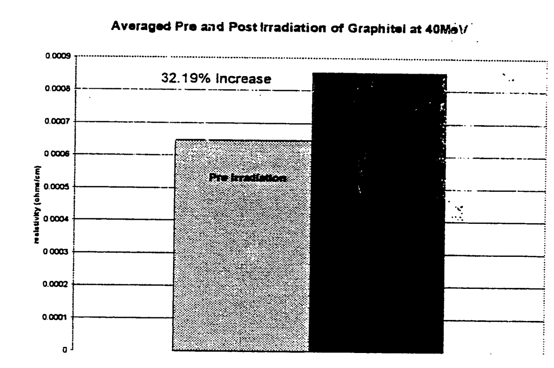
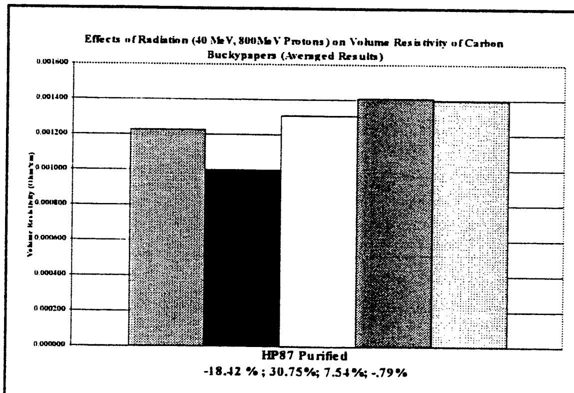
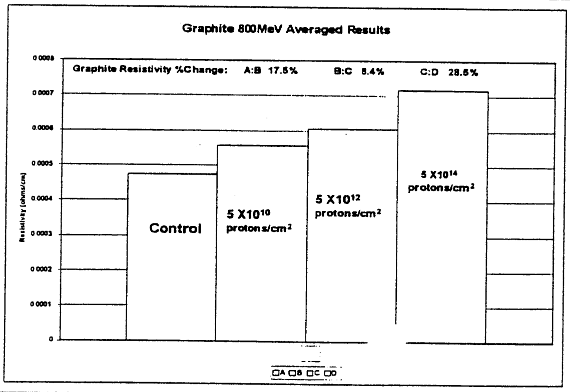
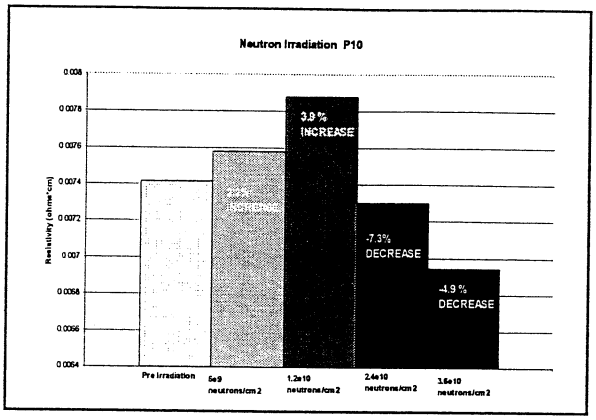
- Materials with higher hydrogen density tend to have better shielding characteristics
- Materials should be radiation resistant to maintain structural integrity
- Carbon Nanotubes fulfill the above requirements for radiation protection shielding materials

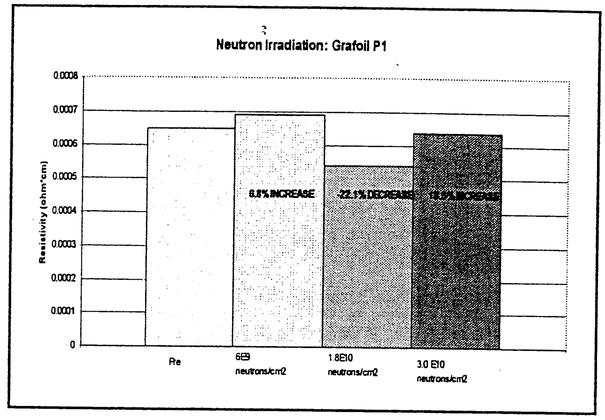












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- Nanotube2002, Boston College
- Dr. Richard Wilkins, Advisor

3.5 Student Speaker Award received by Merlyn Pulikkathara at the 12th Biennial RPSD Topical Meeting of the American Nuclear Society in April 2002

Merlyn Pulikkathara

Prairie View A&M University

Radiation Effects Risk Analysis and Mitigation of Carbon Nanomaterials and Nanocomposites

Richard T. Wilkins, Lovely K. Fotedar, Merlyn Pulikkathara, Harold Huff, Jerry Vera, Enrique Barrera, Robert C. Singleterry, Bashir Syed, and Alice Lee

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In recognition of your participation as a Student Speaker

AMERICAN NUCLEAR SOCIETY

Radiation Protection & Shielding Division

12th Biennial RPSD Topical Meeting

April 14–18, 2002 | Santa Fe, NM