NASA/TM—2003-212209

Microchemical and Gaseous Sensors Using Carbon Nanotubes and MEMS Fabrication Technology

Chung-Chiun Liu
Case Western Reserve University, Cleveland, Ohio

Randy Vander Wal
National Center for Microgravity Research, Cleveland, Ohio

Gary Hunter
Glenn Research Center, Cleveland, Ohio

April 2003

The NASA STI Program Office . . . in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the Lead Center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- TECHNICAL PUBLICATION. Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA's counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.
- TECHNICAL MEMORANDUM. Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.
- CONTRACTOR REPORT. Scientific and technical findings by NASA-sponsored contractors and grantees.
- CONFERENCE PUBLICATION. Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.
- SPECIAL PUBLICATION. Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.
- TECHNICAL TRANSLATION. English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized databases, organizing and publishing research results . . . even providing videos.

For more information about the NASA STI Program Office, see the following:

- Access the NASA STI Program Home Page at ***http://www.sti.nasa.gov***
- E-mail your question via the Internet to help@sti.nasa.gov
- Fax your question to the NASA Access Help Desk at 301–621–0134
- Telephone the NASA Access Help Desk at 301–621–0390
- Write to:
  NASA Access Help Desk
  NASA Center for AeroSpace Information
  7121 Standard Drive
  Hanover, MD 21076

NASA/TM—2003-212209

Microchemical and Gaseous Sensors Using Carbon Nanotubes and MEMS Fabrication Technology

Chung-Chiun Liu
Case Western Reserve University, Cleveland, Ohio

Randy Vander Wal
National Center for Microgravity Research, Cleveland, Ohio

Gary Hunter
Glenn Research Center, Cleveland, Ohio

National Aeronautics and
Space Administration

Glenn Research Center

April 2003

The Propulsion and Power Program at
NASA Glenn Research Center sponsored this work.

Available from

NASA Center for Aerospace Information
7121 Standard Drive
Hanover, MD 21076

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22100

Available electronically at http://gltrs.grc.nasa.gov

Microchemical and Gaseous Sensors Using Carbon Nanotubes and MEMS Fabrication Technology

Chung-Chiun Liu
Electronics Design Center
Case Western Reserve University
Cleveland, Ohio 44106

Randy Vander Wal
National Center for Microgravity Research
Cleveland, Ohio 44135

Gary Hunter
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

This research is a joint effort between the researchers in the Electronics Design Center at Case Western Reserve University and the National Center of Microgravity Research (NCMR)/ Universities Space Research Association at NASA Glenn Research Center. The overall objective is to advance nanosensor technology for gaseous detection in propulsion and power systems for aerospace applications. The underpinning technology of this research is a combination of silicon-based microfabrication and micromachining processes and carbon nanotube technology.

In this research, photolithography and thin film metallization techniques were used to produce the basic sensor structure. This metallic sensor structure also served as the catalytic precursor for the formation of carbon nanotubes. Metals such as Fe, Ni and Co were the candidates for the catalytic precursor. An ion beam sputtering system was used to carry out the metallic thin film deposition.

Even though the grant started late and both research groups had delays due to laboratory renovation and equipment modifications, we have made excellent progress towards our research goals in the first year and second year. Specifically, we have carried out the following tasks successfully:

1. We identified nickel and cobalt to be the metallic catalysts appropriate for CNT synthesis. Accordingly sputtering targets for these metals were acquired. Different metal screen meshes and foils were used as the substrates for the deposition to test the suitability of these catalysts. The thickness of the deposition varied, including 5, 10, and 20 nm.
2. Polished quartz discs were chosen as potential sensor substrates for the study. The disc was approximately 1 cm in diameter and finely polished. Two types of metallic depositions were carried out. In the first type of deposition, the whole surface area of the disc was covered with deposited metal. Pure nickel and pure copper were deposited by the sputtering technique. A thickness of 20 nm pure nickel deposited on the top surface of 20 nm pure copper of a quartz disc was also undertaken. These deposited metallic films were then used as the sites for the growth of carbon nanotubes were then assessed.

The second type of deposition was carried out on patterned sensor structures on a quartz disc. Figure 1 shows the design of the sensor structure that has an interdigitated configuration. The design structure was then deposited onto 1 cm diameter quartz discs. Cobalt in the thickness of 5, 10 and 20 nm were deposited using a shadow mask. These structures are planned to be used for the growth of carbon nanotubes. The carbon nanotube covered sensor structures will then be ready for evaluation as a gaseous sensor.

3. Silicon carbide is a high temperature electric material. It has been considered as a potential sensor material that may be used in high temperature hazardous environments. In our study, the growth of carbon nanotubes on silicon carbide substrates was also countertubes. The process is a combination of catalyst reduction and carbon nanotube synthesis conditions. The characterization of the growth density and the uniformity arrayed SiC fibers supporting carbon nanotubes upon SiC are shown in Figs. 2 to 4 respectively.

Stainless steel mesh deposited with metal catalyst for the growth of carbon nanotubes were also carried out in order to test CVD or flame synthesis conditions. We may point out that the flame process is unique in the growth of carbon nanotubes. Figure 5 shows the results obtained. Figure 6 shows the coated quartz disc using chemical vapor deposition also. The results are not very good indicating a relatively poor combination of CVD and catalyst choice. Choice of catalyst and synthesis conditions matter!

Modifications on the experimental conditions were undertaken. Figure 7 and 8 shows the foundation of carbon nanotubes upon SiC, under modification, are more favorable. Figures 9 and 10 show the foundation of carbon nanotubes on stainless steel mesh under modified synthesis conditions. Figure 11 shows the growth of carbon nanotubes on a nickel-covered copper foil to explore synergy with sensor contacts. This was done using the flame-based synthesis technique.

The following images represent the best combination of catalyst, support and CNT growth conditions. Therein they should not be compared to each other for judging the relative merits of these parameters. The number of images, corresponding to the below conditions are presented in the report in order to illustrate the variety of final products that we have successfully synthesized to-date. Therefore, there are some specific points to be made regarding each sample. These are succinctly made in the caption for each figure.

Combinations of conditions that did not work are generally not shown in this report, with the exception of Fig. 6. This image is rather representative of all that did not work as such tests usually resulted in few if any CNTs upon a rather barren substrate.

To capture the synthesis tests conducted to-date, we have found our flame synthesis process to be optimum for catalysts (Co for now) supported on SS mesh. There is a small range of flame equivalence ratios that lead to excellent CNT growth (as judged by uniformity of diameter, lengths, areal density). The optimum catalyst for SiC fiber is either Ni or a Ni/Cu mixture. The best synthesis vehicle is thermal CVD using the mixture as indicated for sample no. 6.

Sample	Material	Catalyst	Treatment Reduction/Growth
1 (Fig. 2)	SiC fibers	Fe/Cr/Ni/Mn mixture	R & G1
2 (Fig. 3)	SiC fibers	Cu	R & G2
3 (Fig. 4)	SiC fibers	Cu	R & G2
4 (Fig. 5)	400 SS mesh	Co, 1.0 nm	R & G2
5 (Fig. 6)	Quartz	Cu, 25 nm	R & G2
6 (Fig. 7)	SiC fibers	Cu/Ni mixture	R & G2
7 (Fig. 8)	SiC fibers	Ni	R & G2
8 (Fig. 9)	400 SS mesh	Co, 1.0 nm	G3; phi = 1.62
9 (Fig. 10)	400 SS mesh	Co, 1.0 nm	G3; phi = 1.80
10 (Fig. 11)	Cu foil	Ni, 1 nm	G3; phi = 1.62

Notes:

- G1 corresponds to a C2H2, H2, He environment for CVD
- G2 corresponds to a C2H2/H2/He + benzene gas mixture for CVD
- G3 corresponds to our flame synthesis, using primarily a fuel-rich mixture producing post-flame gases, of which the primary components are CO, H2, H20 and CO2
- Here phi corresponds to the fuel/air equivalence ratio (note that phi > 1 corresponds to fuel-rich conditions, i.e. incomplete combustion.)

These experimental results devised directly from a combination of carbon nanotubes and microfabrication techniques. Preliminary results provide guidance for the selection of synthesis conditions for the carbon nanotubes on a defined sensor structure. We anticipate substantial results will be derived in the forthcoming years.

Because of the issues involved in the laboratory renovation and the equipment maintenance, we have altered some of our research goals in the first and second years. In summary, we have done substantial research on the growth of carbon nanotubes on SiC. Also, the design and fabrication on the sensor structure (originally planned for the second year) have been moved forward and undertaken in this year. We made adjustments in order to maximize our research efforts.

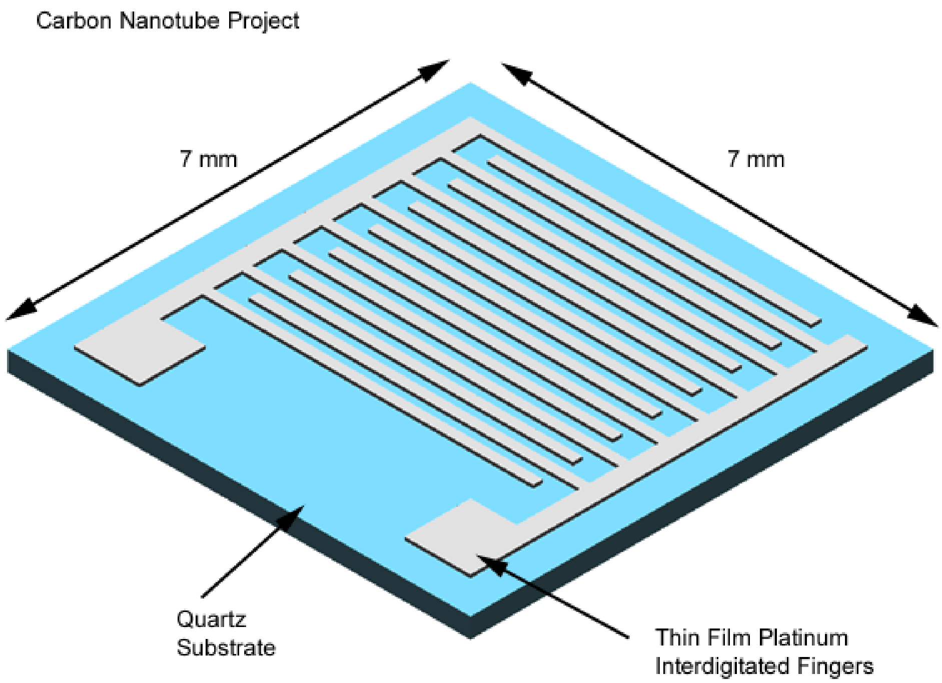

Figure 1. Configuration of the interdigitated sensor structure
on which carbon nanotubes will be grown.

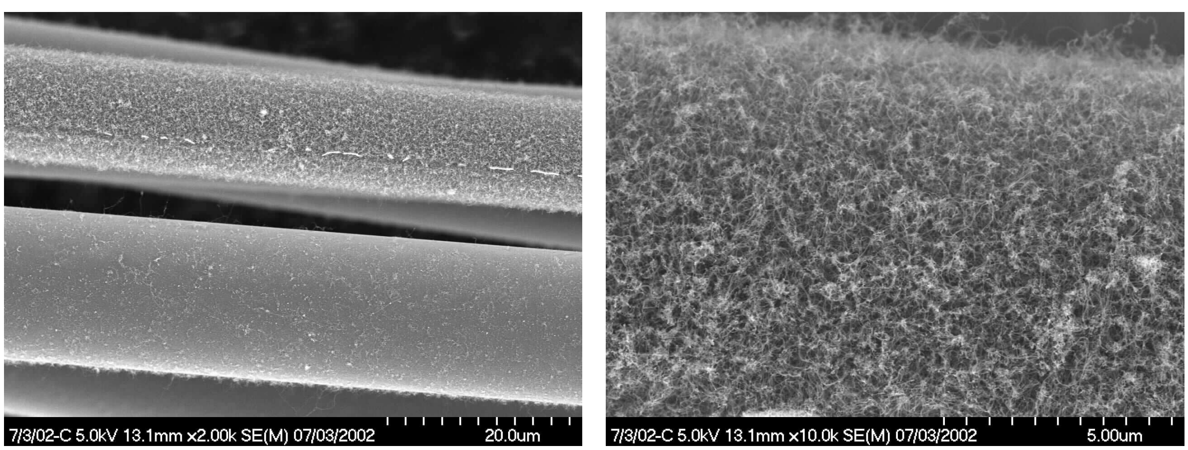

Figure 2. Carbon nanotubes upon SiC showing initial variability in the CVD processing.

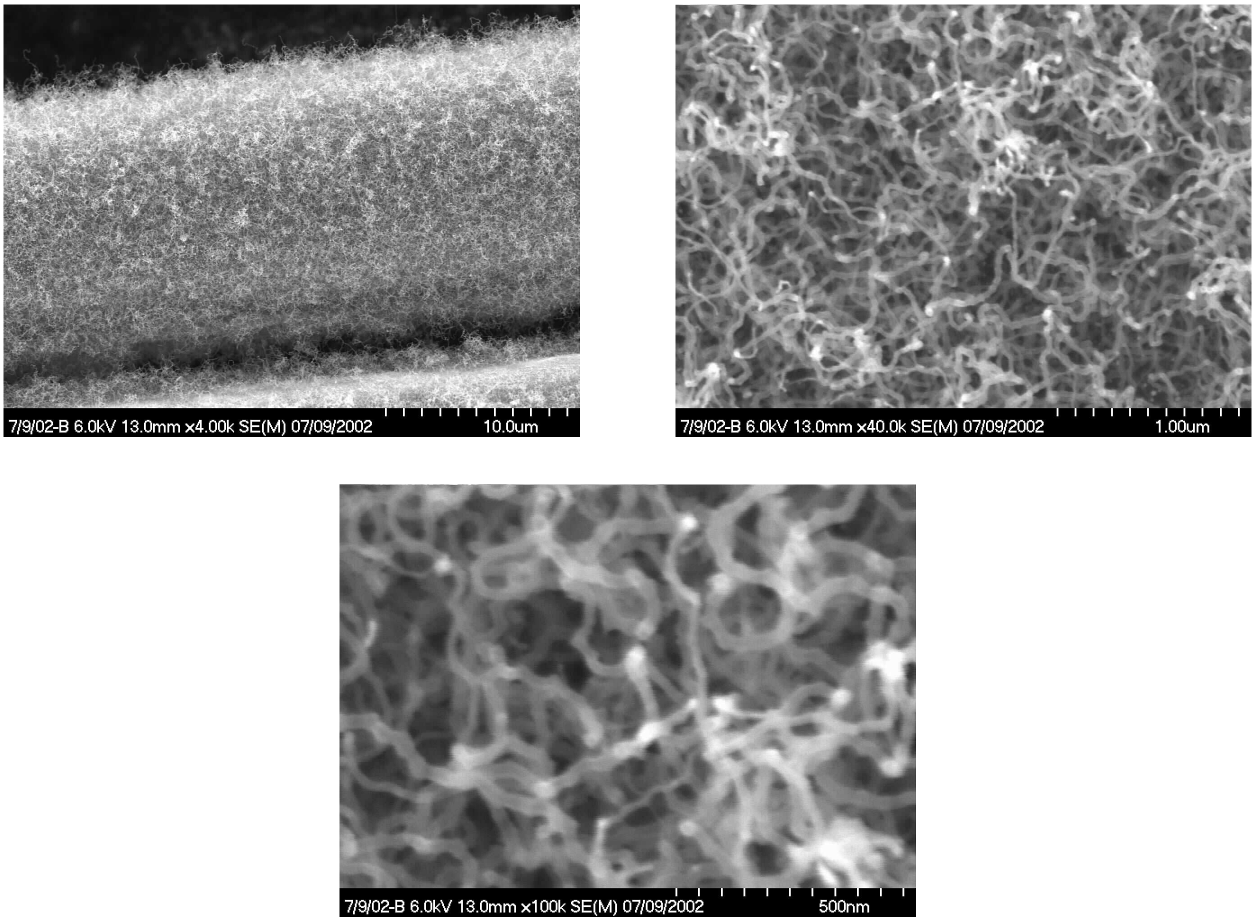

Figure 3. Carbon nanotubes upon SiC illustrating the density of growth.

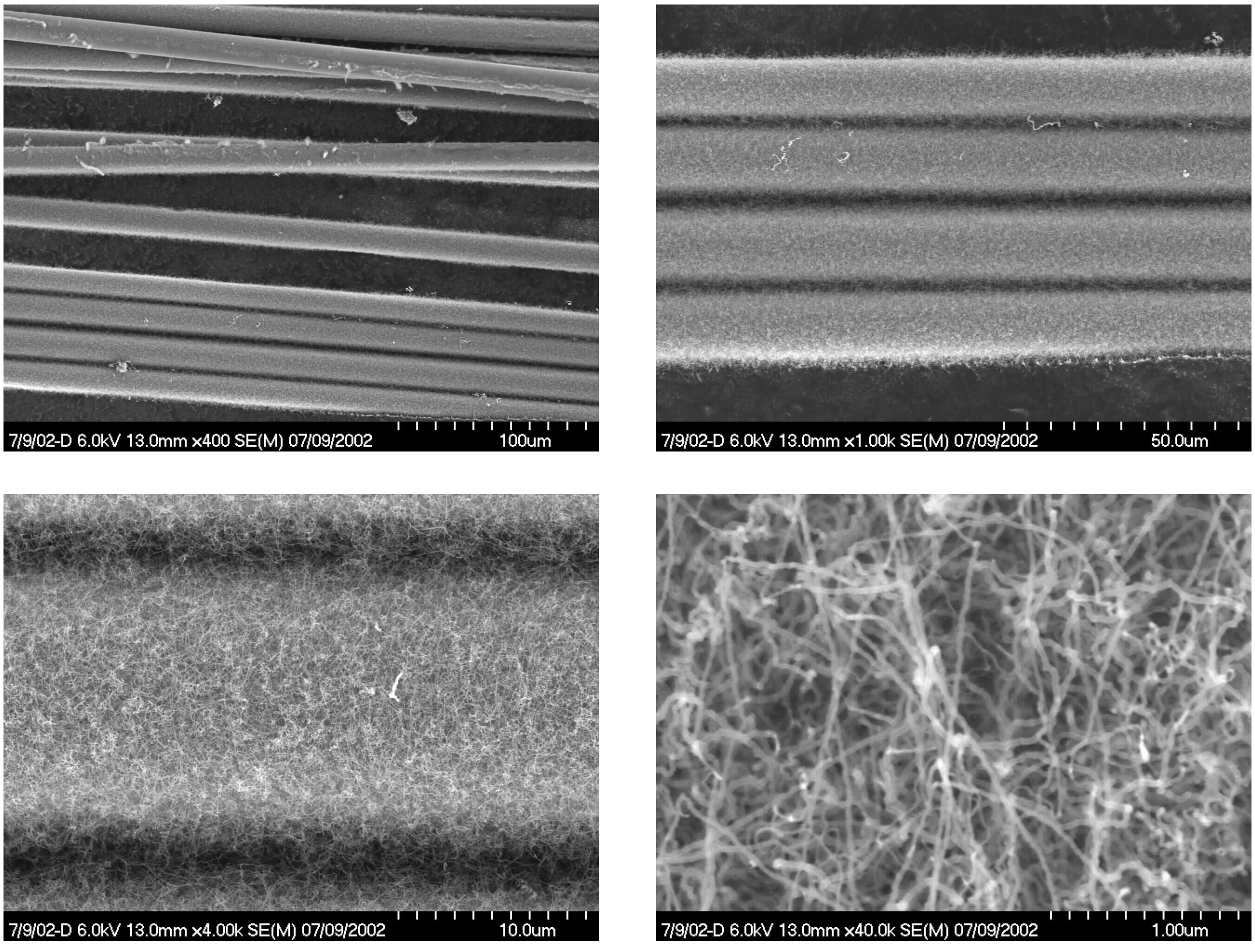

Figure 4. Uniformly arrayed SiC fibers supporting carbon nanotubes upon SiC.

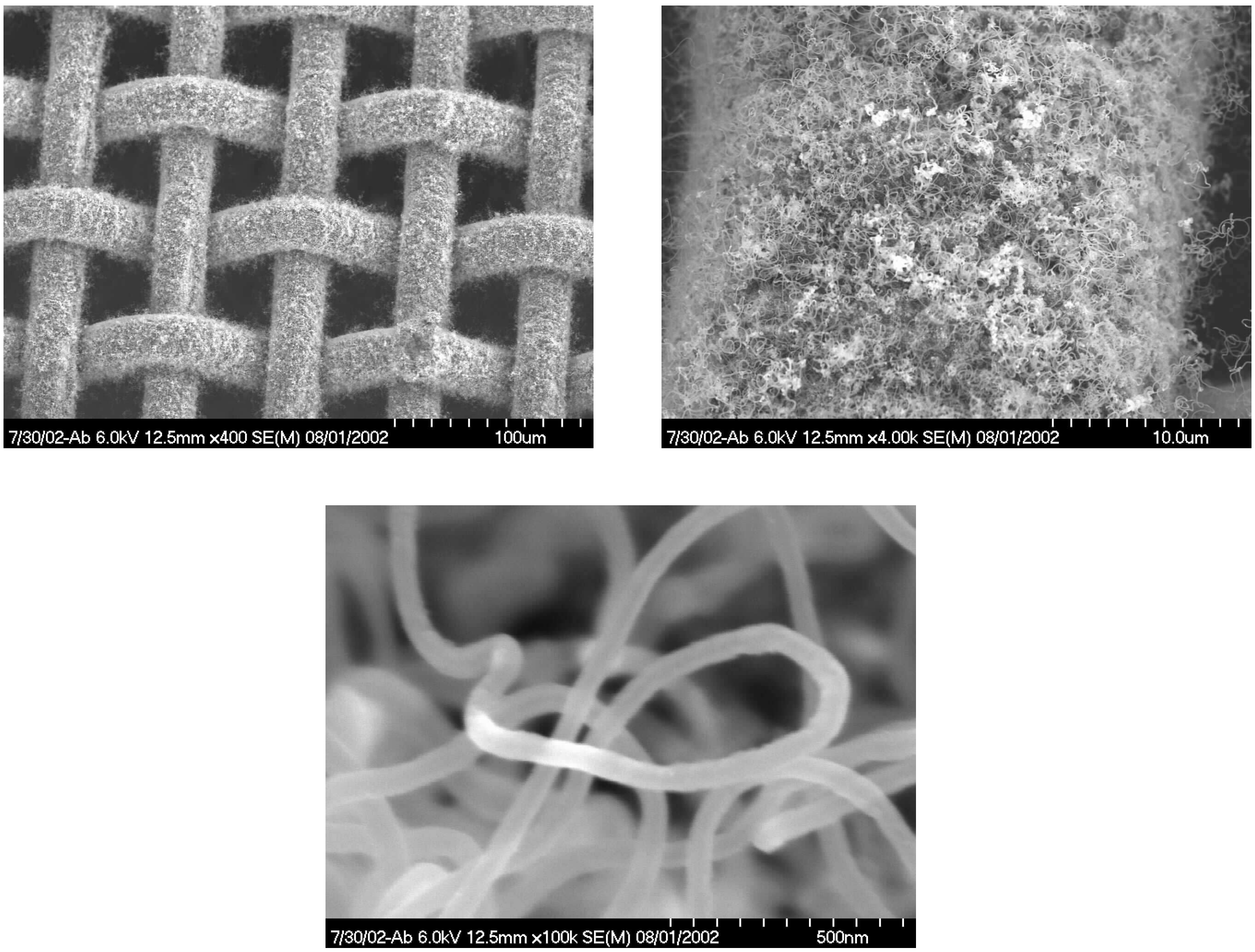

Figure 5. Carbon nanotubes upon SS mesh for identifying CVD and catalyst combinations.

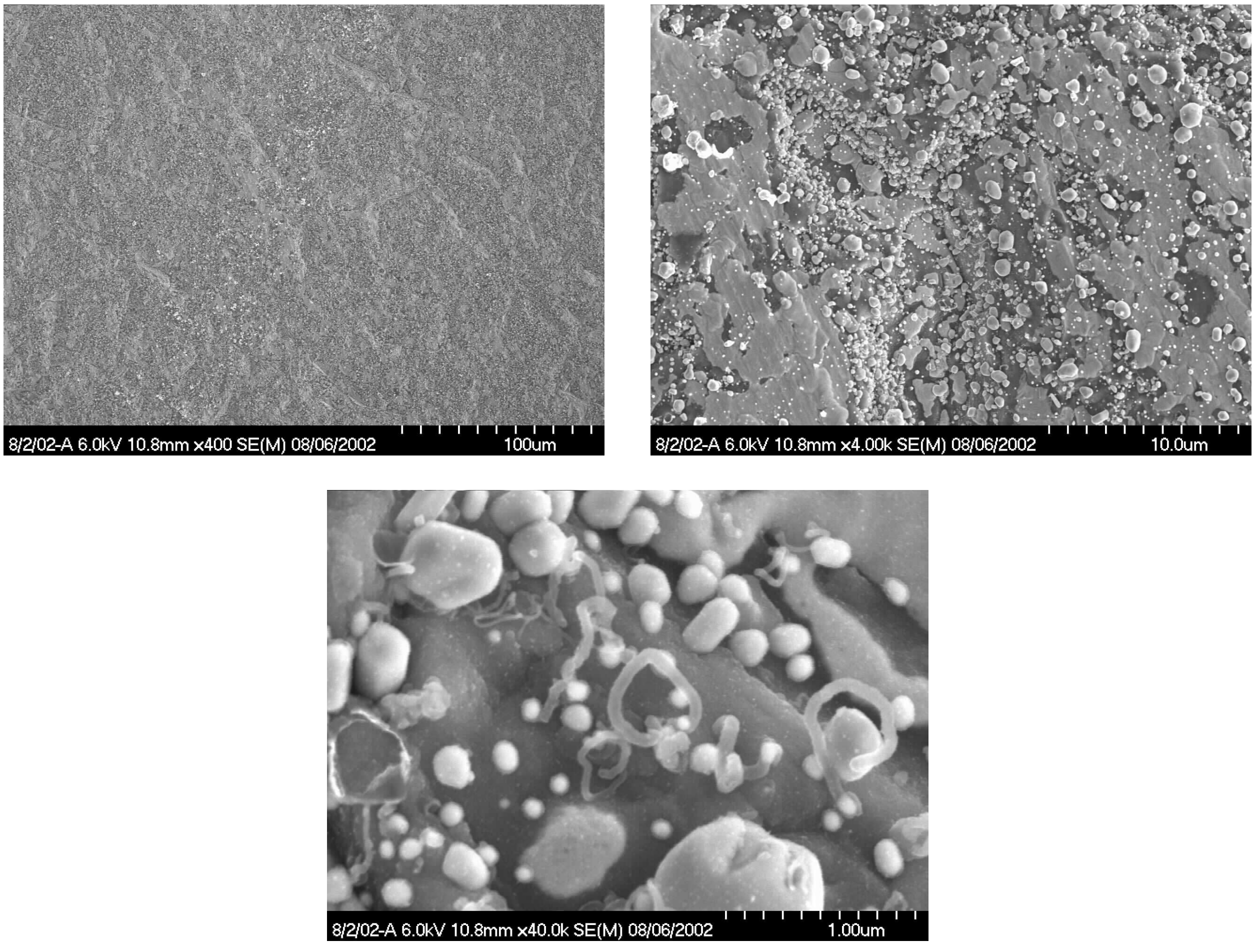

Figure 6. Carbon nanotubes Cu coated quartz illustrating a poor combination of CVD and catalyst choice.

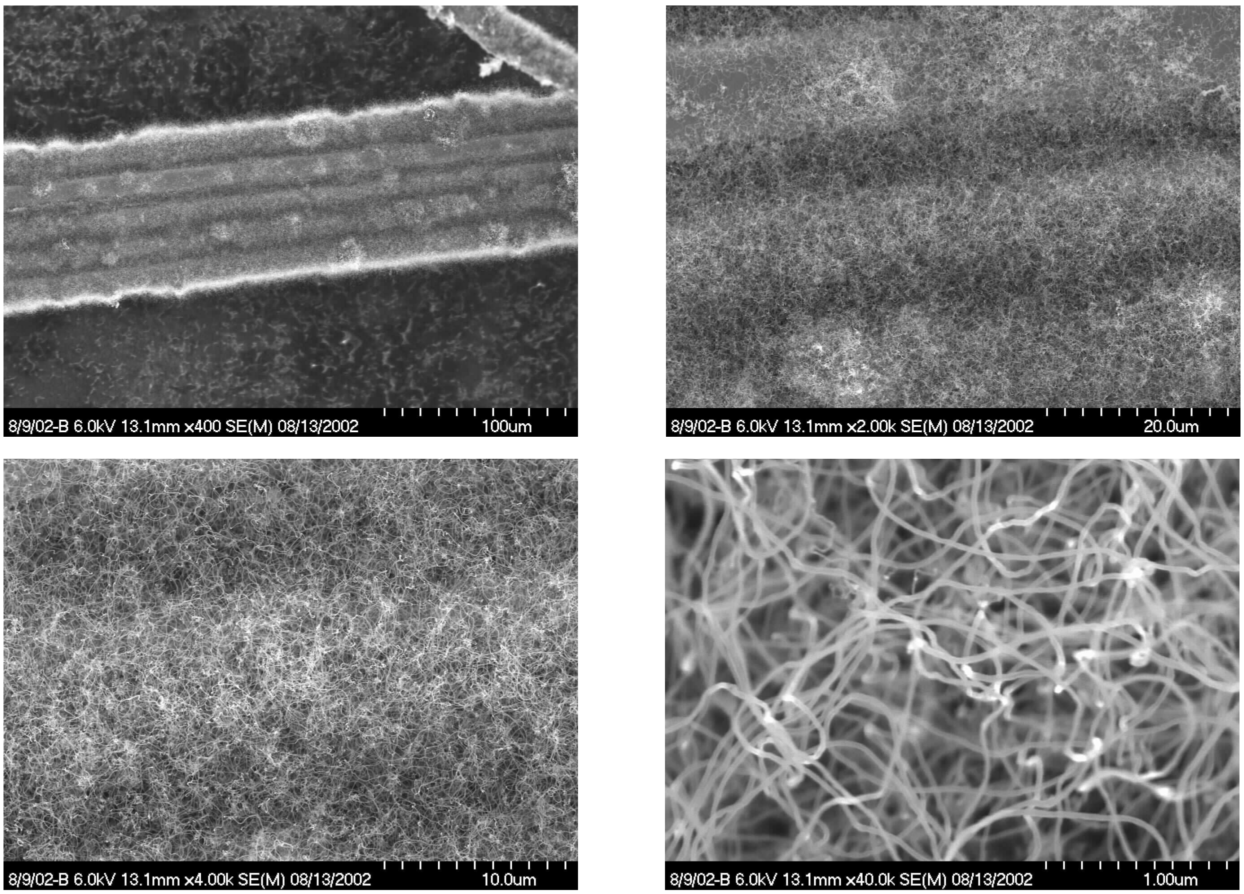

Figure 7. Carbon nanotubes upon SiC using optimum synthesis conditions.

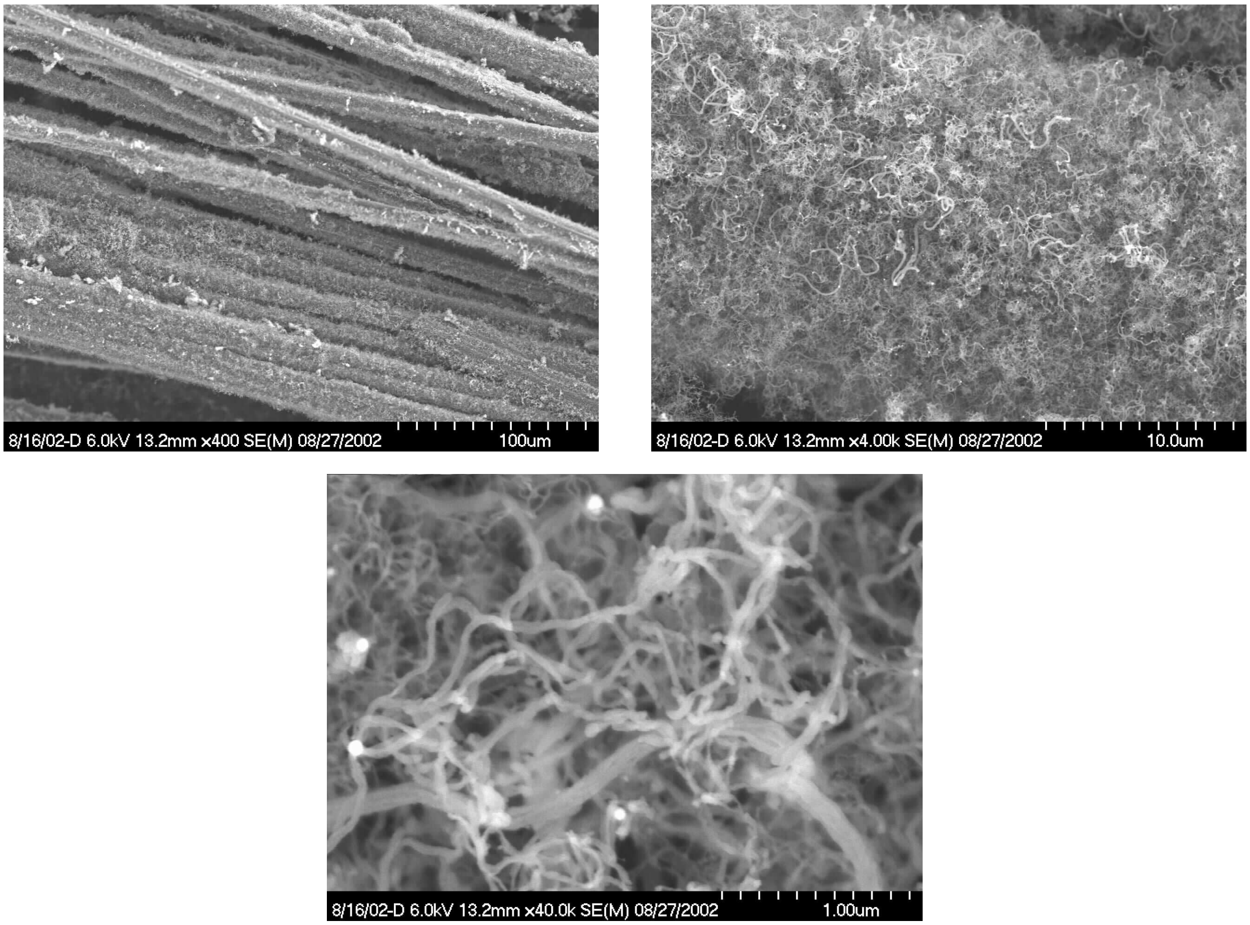

Figure 8. Carbon nanotubes upon bundled tow of SiC.

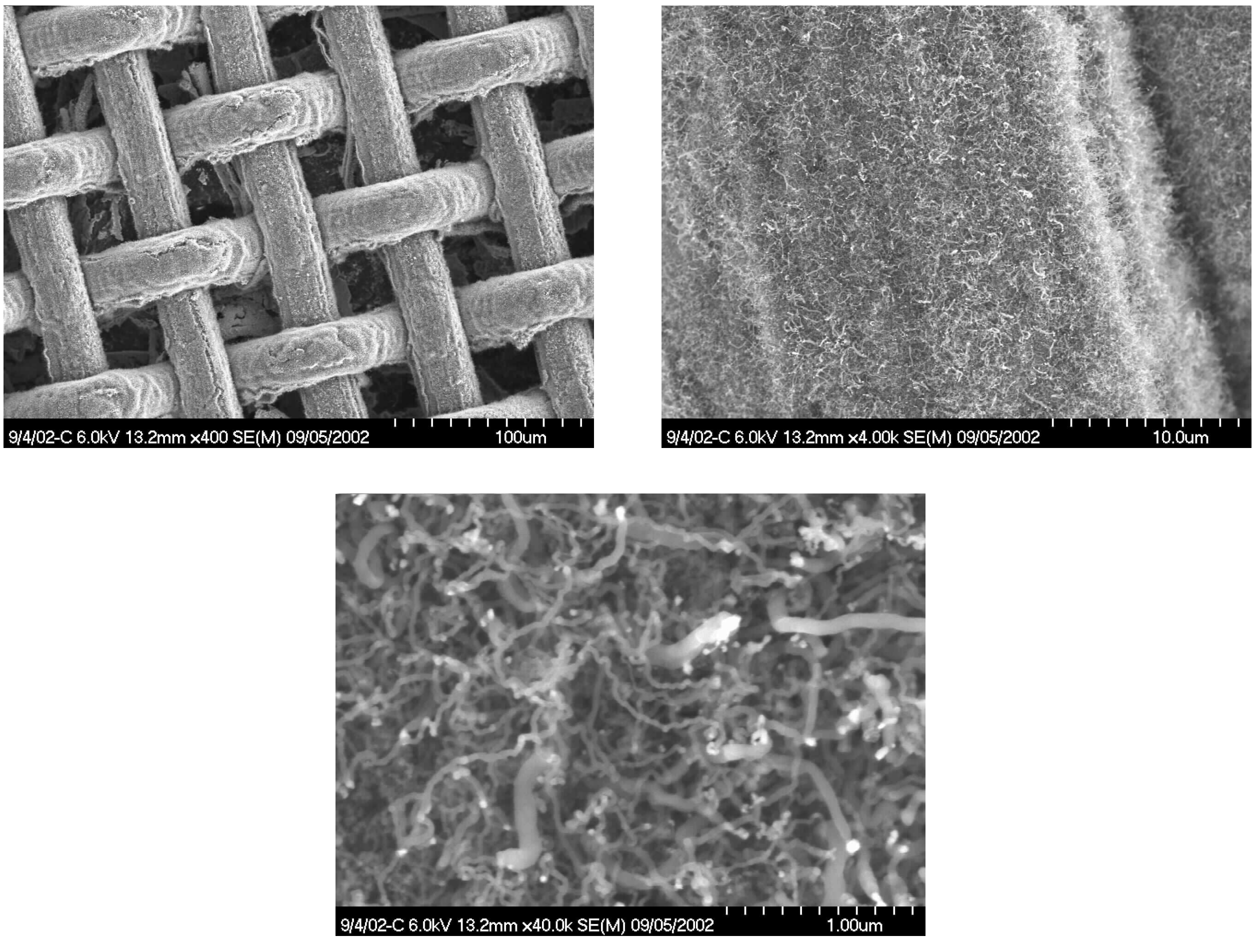

Figure 9. Carbon nanotubes upon SS mesh to guide synthesis conditions for CNTs.

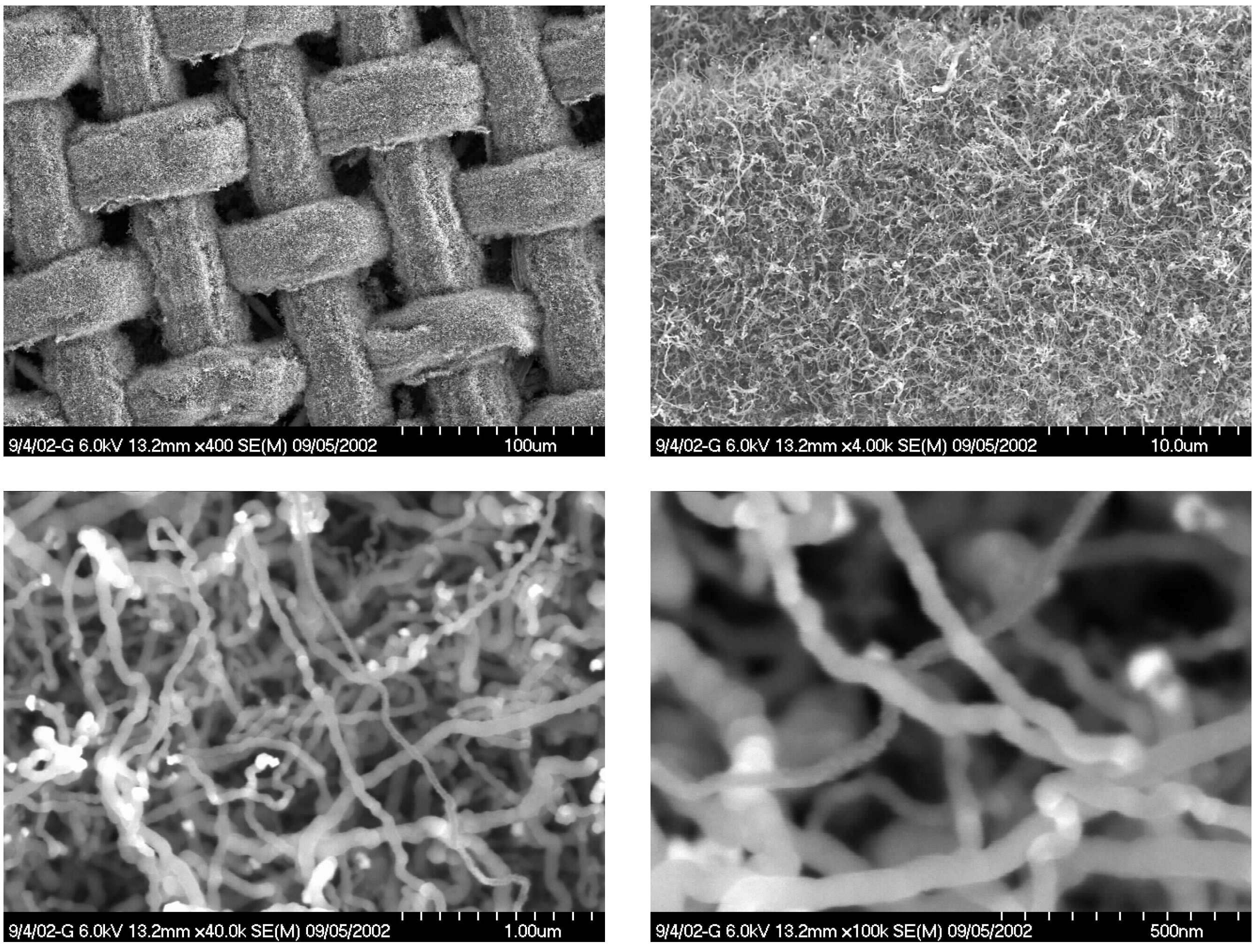

Figure 10. CNTs upon SS mesh under optimum synthesis conditions.

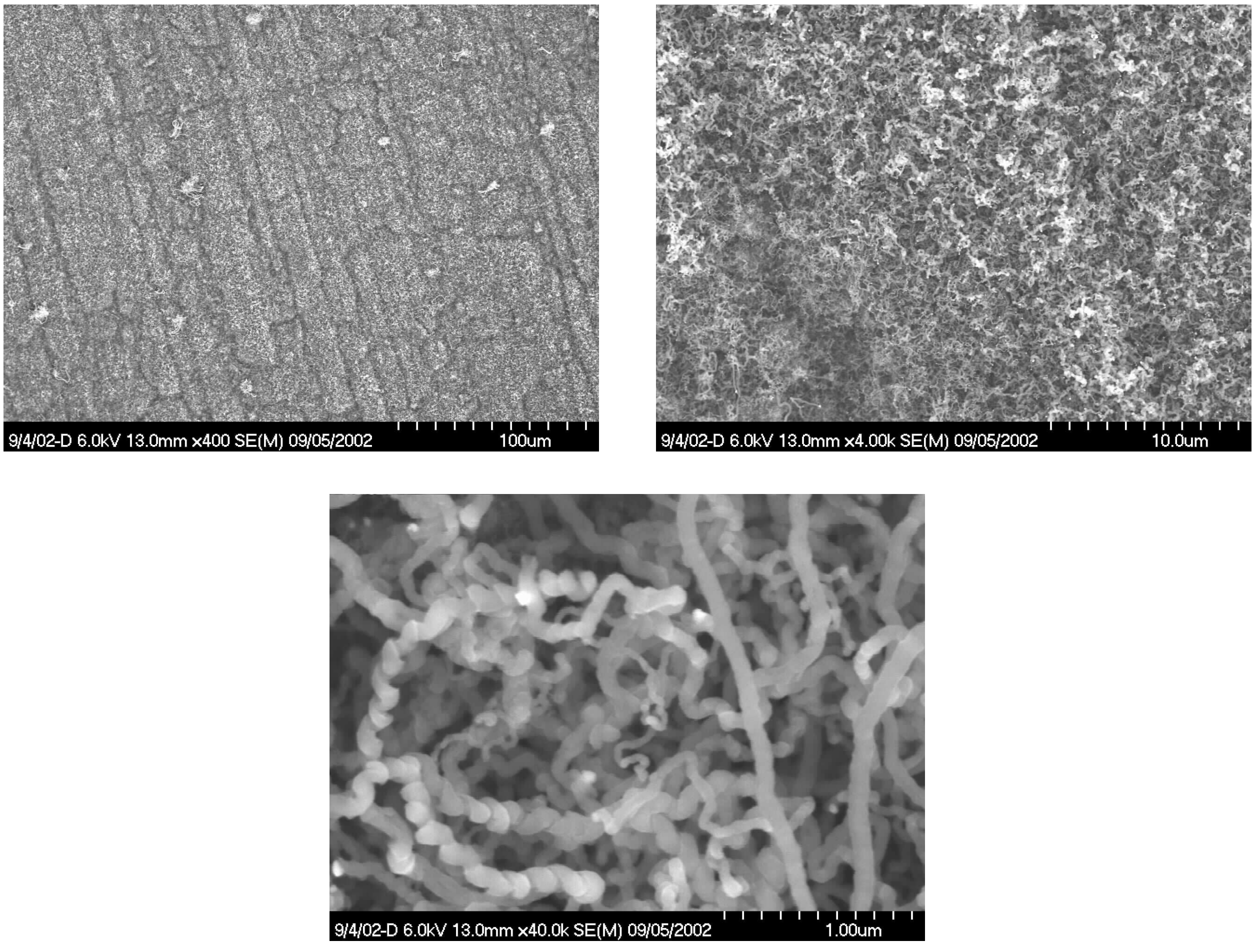

Figure 11. CNTs upon Cu foil to explore synergy with sensor contacts.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave blank*)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	April 2003	Technical Memorandum

4. TITLE AND SUBTITLE

Microchemical and Gaseous Sensors Using Carbon Nanotubes and MEMS Fabrication Technology

5. FUNDING NUMBERS

WU–708–87–23–00

6. AUTHOR(S)

Chung-Chiun Liu, Randy Vander Wal, and Gary Hunter

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
John H. Glenn Research Center at Lewis Field
Cleveland, Ohio 44135–3191

8. PERFORMING ORGANIZATION REPORT NUMBER

E–13817

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, DC 20546–0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM—2003-212209

11. SUPPLEMENTARY NOTES

Chung-Chiun Liu, Case Western Reserve University, Cleveland, Ohio 44106; Randy Vander Wal, National Center for Microgravity Research, Cleveland, Ohio 44135; and Gary Hunter, NASA Glenn Research Center. Responsible person, John D. Wrbanek, organization code 5510, 216–433–2077.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Categories: 01 and 07 Distribution: Nonstandard

Available electronically at http://gltrs.grc.nasa.gov

This publication is available from the NASA Center for AeroSpace Information, 301–621–0390.

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 words)***

The objective of this research is to use a combination of carbon nanotubes and silicon-based microfabrication and micromachining processes to produce unique micro-sized chemical and gaseous sensors. Polished quartz substrate is used. Interdigitated structure is used for the sensing elements. Metallic catalysts for the growth of the carbon nanotube include copper, iron, nickel, and cobalt. Various thicknesses of the metallic catalysts are used in this study varying between 5 to 20 µm. Depositing of the metallic catalyst is accomplished using an ion-beam sputtering thin film technique and a shadow mask. Single wall carbon nanotubes are successfully formed over the metallic catalyst layer. Preliminary measurements of the carbon nanotubes show this nanotube contained film over the sensing elements which had a resistance value of 400 ohms at room temperature. This is a more conductive film comparing to metal oxide films, such as SnO_2 or ZnO, that are now widely used in gaseous sensor research. Evaluation of the carbon nanotube film for potential gaseous sensing will be carried out.

14. SUBJECT TERMS

Carbon nanotubes; Sensor; Microfabrication

15. NUMBER OF PAGES

19

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	