REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
30-10-2014	Final Report	1-Aug-2012 - 31-Jul-2014

4. TITLE AND SUBTITLE
Final Report: In-situ, Nanosecond, High Resolution TEM Instrumentation for Multi-Disciplinary Research and Education in Nanomaterials

5a. CONTRACT NUMBER
W911NF-12-1-0366

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611103

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
61581-CH-RIP.1

12. DISTRIBUTION AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
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15. SUBJECT TERMS
in situ mechanical testing, transmission electron microscopy, double tilt, nanowires, carbon nanotube, sample platform

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
UU	UU	UU	UU		Horacio Espinosa
					19b. TELEPHONE NUMBER
					847-/46-7598

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

Report Title

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Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u> <u>Paper</u>

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u> <u>Paper</u>

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Espinosa - Elected Fellow of American Association for the Advancement of Science, 2013

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Rodrigo Bernal	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Horacio Espinosa	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

In-situ, Nanosecond, High Resolution TEM Instrumentation for Multi-Disciplinary Research and Education in Nanomaterials

PI: Horacio D. Espinosa
Northwestern University

Abstract

This DURIP instrumentation grant allowed us to develop new instrumentation that significantly improved experimental capabilities to characterize the mechanical properties of carbon nanotube and metallic nanowire materials. In particular, the purchased equipment included a nanomanipulator for preparation of nano-specimens for in-situ Scanning Electron Microscopy (SEM). The objective of the manipulator was to provide a sample preparation platform for specimens that will subsequently be tested by in-situ SEM or Transmission Electron Microscopy (TEM). In addition, a double-tilt, electrical biasing, TEM specimen holder was designed by us and custom fabricated. The electrical biasing capabilities allow the TEM holder to operate microelectromechanical system (MEMS) devices previously developed by our group for mechanical testing of nanostructures. The two combined instruments therefore provide a system for mechanical testing of nanostructures, combining capabilities of: (1) double-tilting in TEM for accurate structural characterization, (2) MEMS testing of nanostructures in-situ TEM, affording high resolution in loads and (3) straightforward sample preparation for TEM and SEM testing of nanostructures.

Statement of the problem studied

In our lab, we have an array of projects related to the in-situ electron microscopy mechanical and electromechanical testing of nanomaterials. Recent focus areas have been carbon nanotube (CNT) –based hierarchical nanocomposites, and fundamental properties of metallic and semiconducting nanowires. Both of these materials are important components of future advanced materials and electronic systems.

In particular, the mechanics of carbon nanotubes and carbon nanofibers and their application to advanced yarns and composites are investigated. Emphasis is placed on characterizing and improving load transfer in nanotube-reinforced fibers and composites through polymer and covalent-bond mediated inter- and intra-tube cross-linking. On the other hand, nanowire (NW) materials, which are envisioned to be the building blocks of future electronic systems, are studied. In-situ Transmission Electron Microscopy (TEM) experiments are complemented by atomistic and multi-physics simulation to establish failure mechanisms, mechanical properties, and electromechanical coupling in these nanostructures.

This document reports the results of a DURIP instrumentation grant that allowed us to develop new instrumentation that will result in significantly-improved experimental capabilities to characterize the aforementioned materials.

Summary of the most important results

1.1 Acquisition of Attocube nanomanipulator

An Attocube ECS3030 nanomanipulator and related accessories for in-situ SEM sample preparation of nano-specimens was acquired. This manipulator allows movement of a tungsten probe over several millimeters with sub-nanometer resolution, and with additional accessories, also rotation about its own axis, resulting in four degrees of freedom. These capabilities make this instrument extremely useful for sample preparation and nanomanipulation of nanostructures such as Carbon Nanotubes (CNTs) and nanowires (NWs), inside an SEM. Its modularity, degrees of freedom and ease of operation constitutes a significant advantage over current instrumentation, decreasing sample preparation time and effort which translates to a higher throughput of successful in-situ SEM/TEM testing.

The basic nanomanipulator is depicted in Figure 1a. The movement is achieved by three individual piezoelectric actuators, one for each axis. The nanomanipulator has a tool-holder in which a tungsten tip can be mounted (Figure 1b). The instrument sits within the SEM chamber (Figure 1b) attached to the sample stage by an adapter plate. Cables for operation are routed through a vacuum feedthrough (Figure 1c). These cables are then connected to a control box (Figure 1d), which interfaces via USB with a computer or a joystick for operation of the manipulator.

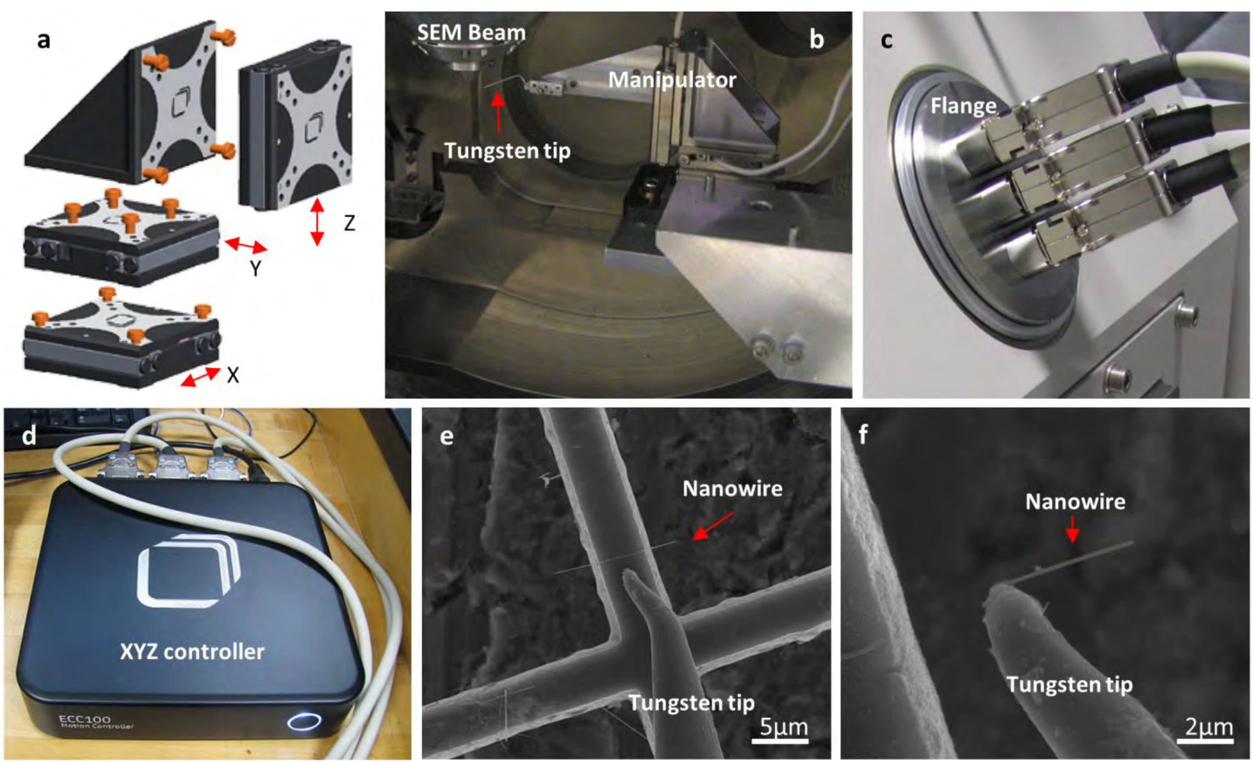

Figure 1

Manipulation of nanowires

One important application of the manipulator is the sample preparation of nanowire specimens for mechanical testing in-situ TEM (enabled, in turn, by the double-tilt holder acquired with this grant). Here, the manipulator is used to transfer a nanowire from the growth substrate (Figure 1e-f) to a MEMS for mechanical testing, which allows tensile loading of the nanowires in-situ TEM (Figure 3e). Figure 1e-f, in particular, show a silver nanowire being picked using the Attocube manipulator. These tests indicated that the resolution and stability of the manipulator is appropriate for this delicate task, as demonstrated by the successful manipulation of the nanowire (Figure 1f).

Peeling studies with nanomanipulator accessories

The modular nature of the manipulator allows interfacing of further actuators or accessories for added functionality. One example of such an accessory is the Attocube rotational actuator (Figure 2a). This actuator has a very small size, and therefore can be moved by an XYZ manipulator, adding another degree of freedom for manipulating nano-specimens. The resolution in rotation is 0.1° yielding good control for manipulating nanostructures. One advantage of the Attocube manipulator over other similar options available in the market (Kleindiek, Omniprobe, Zyvex, Klocke) is the modularity of its components, allowing straightforward upgrades or addition of new plug-ins. This maximizes the functionality and useful life of the system by making it highly adaptable to current and future experiments and capabilities. We expect this system to be useful for current and future projects. Below, we give some examples of its application in current projects.

One potential application of this capability is in the context of our current studies on the peeling behavior of carbon nanotubes as a function of surface chemistry. Such experiments are critical to establish the improvements that surface functionalization have in the lateral interactions between nanotubes in CNT-based hierarchical composites. In the peeling experiment (Figure 2b), a nanotube is attached to an AFM cantilever, allowed to adhere to a substrate, and thereafter peeled from the substrate. The AFM cantilever allows measurement of the peeling force, which can be used to compute the surface energy. These measurements can be carried out for different chemistries of substrate and CNT surface, yielding insights on the most appropriate chemistries for increasing lateral interactions in a CNT-based nanocomposite.

For this experiment, the angles of peeling, and accurate quantification of the CNT length play a critical role in the error of the surface energy estimations. However, it is difficult to establish these geometrical parameters only having a top-view of the experiment, as is typically the case for SEM experiments. However, with the rotating actuator, in addition to moving the cantilever with precision, which is accomplished by the XYZ manipulator, the cantilever can be rotated up to the point where the CNT appears the longest. There, the CNT is parallel to the plane of the image, and the 2D projection of the SEM image is an accurate representation of the geometry of the problem. To demonstrate this capability, Figure 2c shows a 180° rotation of an AFM cantilever chip, enabled by the Attocube rotational actuator.

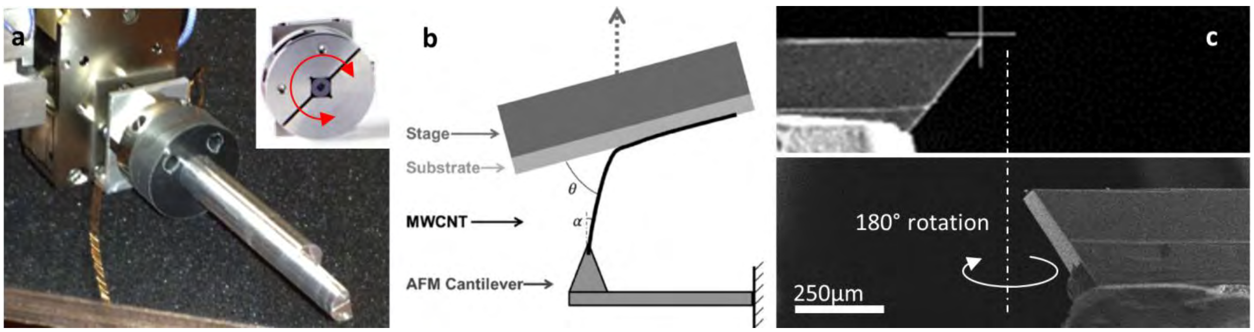

Figure 2

1.2 Acquisition of Double tilt holder for in-situ TEM Mechanical Testing

To complete the experimental suite for testing of nanospecimens, a double-tilt electrical biasing, TEM holder was also acquired from iNfinitesimal LLC. This TEM specimen holder allows the electrical addressing of a chip located in the field of view of the TEM while at the same time providing double tilt capabilities. The TEM holder allows interface with JEOL TEM high-resolution pole pieces. This means that this holder is able to operate in the High-Resolution JEOL 2100F located at Northwestern University, and potentially other laboratories where a JEOL microscopes is available.

In our case, the chip located in the holder contains a MEMS-based nanostructure testing device (Figure 3a), previously demonstrated by our group.

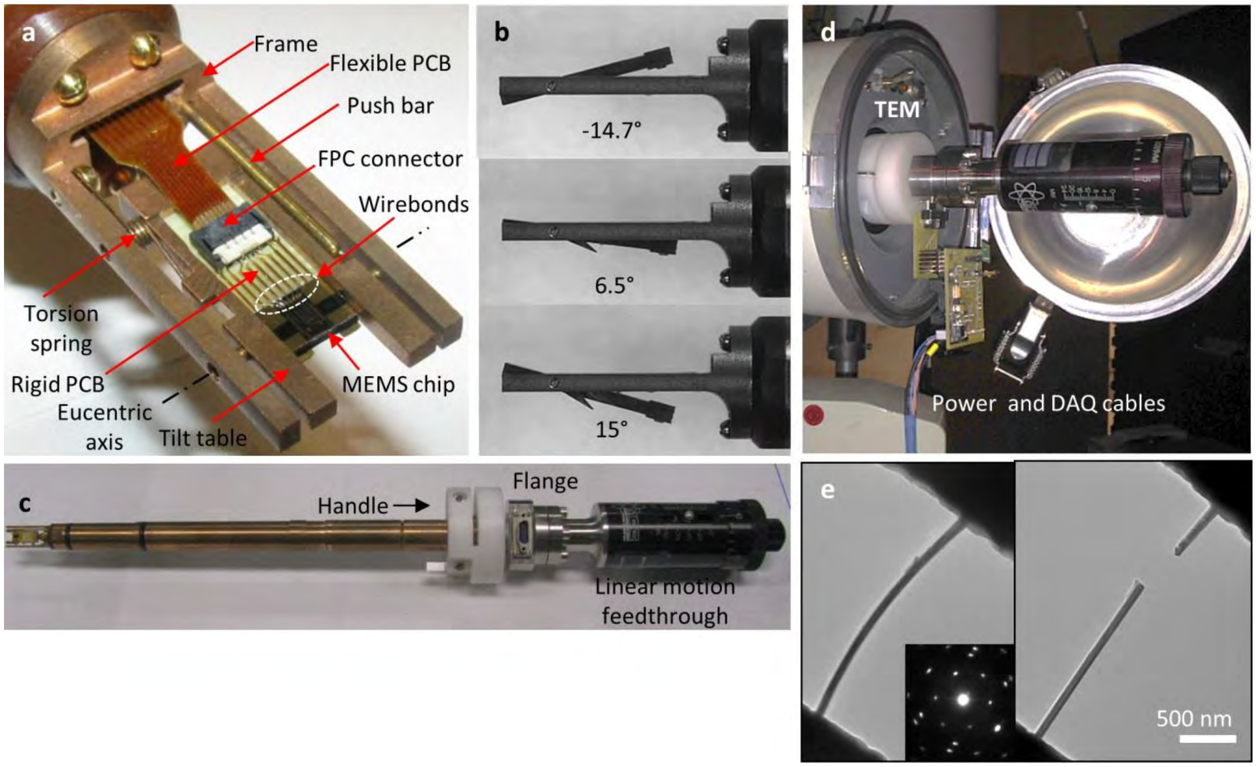

Figure 3

The main components of the holder tip are a frame, and a tilt-table supported on this frame rotating around the eucentric axis (Figure 3a). The tilt table has an incline in contact with a moving bar (called "push bar" hereon). As the bar moves back and forth against the incline, it causes rotation of the tilt table (Figure 3b). A torsion spring pushes the tilt table against the push bar, so that contact is maintained (Figure 3a). The tilt table has a u-shape, a rectangular slot and a set screw, in order to accommodate the electronic assembly that is used to operate the MEMS (Figure 3a).

The electronic assembly is positioned on the tilt table, and allows the connection from the outside electronics to the MEMS chip. A custom-fabricated rigid printed circuit board (PCB) has several parallel traces finished with gold to allow wirebonding to the MEMS chip. One advantage of the design is that only the MEMS chip goes in-between the pole pieces during insertion and operation of the holder.

The FPC connector interfaces with a custom-designed flexible circuit board (Figure 3a), composed of copper conductors patterned on top of vacuum-compatible kapton polymer. The flexibility of this board is important so that it does not hinder rotation of the tilt-table. The flexible PCB extends into the hollow holder shaft, and interfaces at the other end of the holder (Figure 3c) with a commercial connector (Figure 3d).

On the other hand, the tilting mechanism, as alluded to before, is actuated by a push-rod. The push rod is coupled to an internal bar, located inside the hollow holder shaft. This bar in turn is coupled to a linear-motion, ultra-high-vacuum feedthrough, which couples to the flange and provides precise linear motion (0.025mm resolution) by rotating a knob (Figure 3c).

The double tilt holder was applied to carry out tensile tests of silver nanowires in-situ TEM (Figure 3e). This figure shows the nanowire before testing and after fracture has occurred. The double tilting capabilities allowed the capture of a low-index diffraction pattern, as shown in Figure e-inset.

Note that this holder was developed as a customized item for our group and therefore is the first in the world to integrate capabilities of more than 4 electrical connections and double tilting. As such, we expect this holder to also be useful for a host of other applications such as thermal or electrical testing where several electrical connections are needed to operate devices or heaters inside the TEM. A manuscript is near completion and will be submitted before the end of 2014 to disseminate the capabilities of this holder to the research community.

Opportunities for training

Three graduate students have been trained and become proficient in various parts of the instrumentation, not only in operation, but also in technical aspects such as the design and optimization of the electronics. Such technical training will be useful for their future research and careers. In particular, Mr. Mike Roenbeck, Mr. Rajaprakash Ramachandramoorthy and Dr. Rodrigo Bernal have all been trained in nanomanipulation protocols. Mr. Ramachandramoorthy and Dr. Bernal have been trained in the use of the double tilt TEM holder.

Miscellaneous equipment purchased

We also purchased an environmental chamber to control the humidity surrounding the microscope that is used for initial sample preparation and a Cascade micromanipulator for manipulating at large scale inside the environmental chamber. Various electronic components and microscope objectives were purchased to complement the major equipment systems reported here.