AFRL-RI-RS-TR-2012-094

NANOTECHNOLOGY SUPPORT FOR MEMRISTOR NANOELECTRONICS

ALBANY COLLEGE OF NANOSCALE SCIENCE
AND ENGINEERING, SUNY ALBANY

MARCH 2012

FINALTECHNICAL REPORT

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
MAR 2012	Final Technical Report	APR 2009 – SEP 2011

4. TITLE AND SUBTITLE
NANOTECHNOLOGY SUPPORT FOR MEMRISTOR NANOELECTRONICS

5a. CONTRACT NUMBER FA8750-09-1-0171
5b. GRANT NUMBER N/A
5c. PROGRAM ELEMENT NUMBER 61102F

6. AUTHOR(S)
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5d. PROJECT NUMBER 2305
5e. TASK NUMBER AL
5f. WORK UNIT NUMBER BN

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8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory/RITB
525 Brooks Road
Rome NY 13441-4505

10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL/RI

11. SPONSORING/MONITORING AGENCY REPORT NUMBER
AFRL-RI-RS-TR-2012-094

12. DISTRIBUTION AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited. PA# 88ABW-2012-1243
Date Cleared: 12 MAR 2012

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Memristive nanoelectronic devices share many of the properties of resistors, as well as the same unit of measure (ohm). However, in contrast to ordinary resistors in which the unit of resistance is permanently fixed, memristance may be programmed or switched to different states based on the history of the voltage applied to the memristance nanomaterial. This project was a unique collaboration between researchers at the College of Nanoscale Science & Engineering (Univ. at Albany) and AFRL/RI to explore the synthesis, nanofabrication, and characterization of memristive devices using nanoscale materials, such as nanoparticles and nanoparticle matrices. The project resulted in the fabrication of single nanoparticle devices which were characterized via conductive atomic force microscopy (cAFM) and electrically switchable nanoparticle-doped films.

15. SUBJECT TERMS
Memristor, CMOS, nanoelectronics, nanomaterials

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
U	U	U	UU	15	JOSEPH E. VAN NOSTRAND

19b. TELEPHONE NUMBER (*Include area code*)
N/A

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1. Summary

The goal of this project was to explore the fabrication and testing of nanomaterials-based memristive electronic devices. The specific tasks of the project included: selection of metal oxides for memristive devices, development of synthesis methods for producing metal oxide nanoparticles, and electrical characterization of nanomaterial-based devices. The major accomplishments of this effort were: 1) development of synthesis methods that resulted in a wide range of size, morphology and crystallinity for titanium oxide and hafnium oxide; 2) investigation of a conductive atomic force microscopy (cAFM) approach for measuring nanoparticle electrical properties, which was used to measure individual nanoparticles; 3) development of techniques to incorporate nanoparticles into nanostructured "vias" and into insulating films; and 4) successful measurement of memristive properties of nanoparticle-loaded insulating films. These results lay the groundwork for follow-on programs that would develop integrated CMOS/memristor hybrid devices.

2. Introduction

The emerging revolution of nanotechnology is expected to stimulate enormous improvements in IT capabilities. Computer architectures are high on the list of technologies that will benefit from nanoscale breakthroughs in the structures, properties, and performance of nanoelectronics. For example, critical feature sizes of a transistor have been less than 100 nm for years, and yet continued reduction in transistor dimensions is expected to continue as new material capabilities as well as new circuit architectures accentuating nanoscale properties are developed. However, the emerging trend in IT-focused nanotechnology development is one that tends to look beyond CMOS technologies. The general consensus in this area is that the fundamental roadblocks for continued enhancement of traditional approaches to transistor scaling and interconnects are soon to limit Moore's Law. Therefore, finding new computer architecture constructs – inventing and developing novel switching and interconnect technologies for processing information, as well as a "bottom up" approach to fabrication – is central to the emerging barrier(s) facing the IC industry. Any new nanotechnology-based approach will initially work in conjunction with CMOS computer architectures, but the development of nanotechnology complementary to CMOS architectures will result in a major shift in IC technology and redefine improvement in commercial and military information systems in ways that far surpass CMOS alone. This research proposal explored an exciting new nanotechnology area that exploits bottom up nanofabrication techniques as well as the recently demonstrated phenomena of memristance [1], an enabling new nanotechnology phenomenon that is being heralded as the fourth fundamental circuit element.

Memristive nanoelectronic devices share many of the properties of resistors, as well as the same unit of measure (Ohm). However, in contrast to ordinary resistors in which the unit of resistance is permanently fixed, memristance may be programmed or switched to different states based on the history of the voltage applied to the memristance nanomaterial. This gives the memristor a hysteresis property in its I-V characteristic. This can be contrasted to ordinary resistors where there is a linear relationship between current and voltage. While similar hysteresis properties have been demonstrated by magnetic materials, these require the presence of large magnetic fields for implementation, which has proven to be a practical limitation to their utilization. Areas such as neuromorphic computing, signal processing, arithmetic processing, and crossbar computing are only some of the potential application areas of memristor nanomaterials. This effort proposed to collaborate with researchers at AFRL/RI to explore the synthesis, nanofabrication, and characterization of nanomaterial-based memristive devices.

3. Methods, Assumptions and Procedures

The specific tasks of the project included: material selection, development of synthesis methods, development of nanoscale electrical characterization methods, and incorporation of nanomaterials into electrical devices. Materials selection and integration flow development was performed in Prof. Cady's lab at CNSE. Current scientific literature was used to guide our materials selection, with emphasis on metal oxides that had previously shown memristive properties. All synthesis was also performed in Prof. Cady's laboratory, using inorganic chemical synthesis techniques. This was done in collaboration with Prof. Magnus Bergkvist (CNSE) and Dr. Joseph Van Nostrand (AFRL/RI), who had previous experience with nanomaterial synthesis.

Integration of nanomaterials into electronic devices was accomplished using two different approaches. In the first approach, nanomaterials were integrated into nanoscale "vias" which had been etched into silicon wafers. Wafer fabrication was performed by the CNSE Center for Semiconductor Research (CSR). These wafers had vias etched into an insulating silicon oxide layer, with an underlying copper electrode. Nanomaterials were coated onto these wafers and excess nanoparticles were removed using a direct contact wiping technique (with a silicone-based applicator). Another approach that was taken was to incorporate nanoparticles into an insulating spin-on glass (SOG) material, hydrogen silsesquioxane (HSQ). These devices were capped with top electrodes using conventional photolithography and then tested using a semiconductor probe station.

Electrical characterization was performed using a variety of methods, including a traditional semiconductor probe station (Agilent 1500 probe station) with associated analysis hardware/software, and also with conductive atomic force microscopy (cAFM). Prof. Cady and his graduate students were assisted by Prof. Rebecca Cortez (Union) and Prof. Robert Geer (CNSE) for the performance of cAFM measurements. We also consulted with Bruker (formerly Veeco) during development of cAFM methods.

4. Results and Discussion

4.1 Key Accomplishments

During this 3-year project, we finished the following tasks:

- Selection, synthesis and characterization of metal oxide nanomaterials
- Electrical testing of individual nanoparticles and nanoparticle aggregates
- Integration of nanoparticles into insulating films and characterization of resulting memristive devices.

4.2 Selection, synthesis and characterization of metal oxide nanoparticles

In this project we selected titanium dioxide and hafnium oxide as the target materials for memristive nanodevices. A thorough survey of current literature indicated that these materials had ideal memristive switching properties and that there were readily available synthesis methods for producing nanoparticles. We used a variety of synthesis methods to yield a range of size, morphology and crystallinity for both materials (Fig. 1). In particular we found that the solvent system and the temperature of the reaction strongly influenced particle morphology and crystallinity. These results were confirmed by dynamic light scattering (DLS), transmission electron microscopy (TEM), and x-ray diffraction (XRD). These particles were then incorporated into nanostructured electrical devices, as well as insulating thin films, to test their electrical behavior. Our hypothesis was that metal oxide nanomaterials would have memristive behavior, like previously-reported thin film devices, but that the exact nature of these devices would be fundamentally different, due to the high uniformity (in crystal structure, phase, etc.) within individual particles. We further hypothesized that aggregates of particles might behave more like thin films than individual particles.

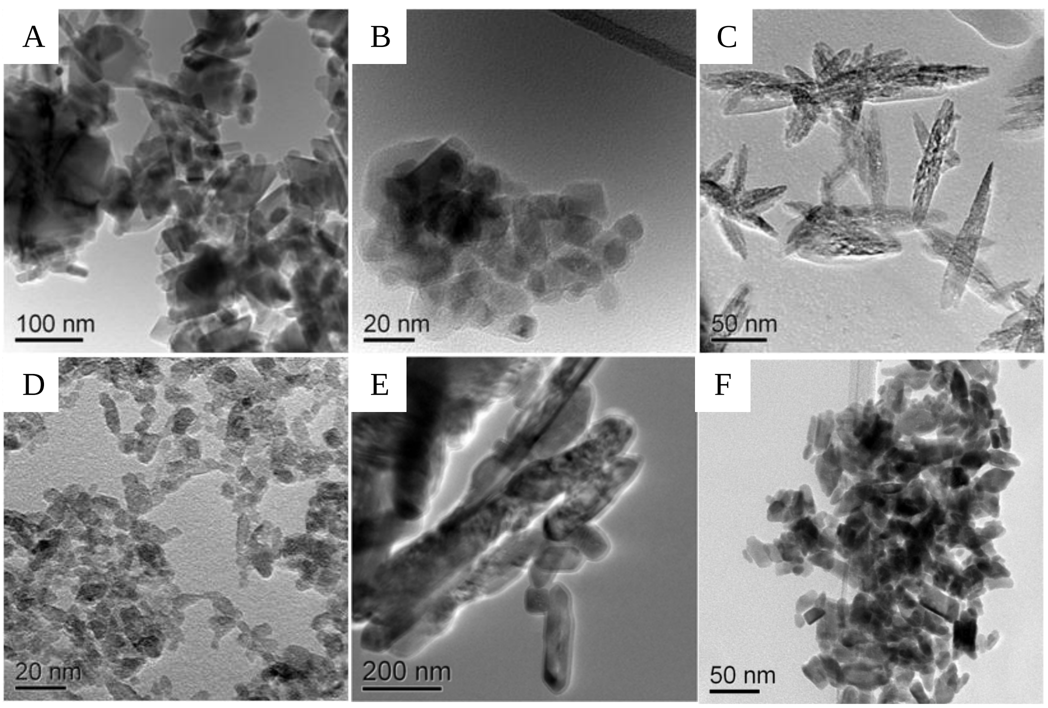

Figure 1: A-D) Anatase TiO_2, E) Rutile TiO_2, and F) Cubic HfO_2 nanoparticles

4.3 Electrical testing of individual particles and particle aggregates

The second result obtained in this work was development of a cAFM strategy for measuring nanoparticle electrical properties. Our initial approach to measuring nanoparticles was to attempt electrical probing with an electron microscope using a nanomechanical electrical probe. This effort was unsuccessful, however, due to difficulties in visualizing the probe and particles within the electron microscope. We therefore converted to an AFM-based approach, in which we could scan the surface with the AFM, making contact with a single particle for electrical measurements. Our cAFM approach utilized conductive AFM probes and the electrical testing module on our Veeco Nanoscope AFM. During this effort we demonstrated that we could both "image" and make electrical contact with metal oxide nanoparticles. However, we could only measure diode-like behavior on individual particles and individual "turn-on" events. We were never able to measure repeatable hysteretic switching events on individual particles. Our efforts included direct interaction with the experimental laboratories for Veeco/Bruker (tool vendor) in which we were able to use their proprietary Peak Force TUNA (PF-TUNE) system. These experiments (using titanium dioxide nanoparticles) demonstrated that we were indeed measuring highly resistive individual nanoparticles and that the "turn-on" event that we were seeing was indeed an electro-mechanical breakdown of the particle.

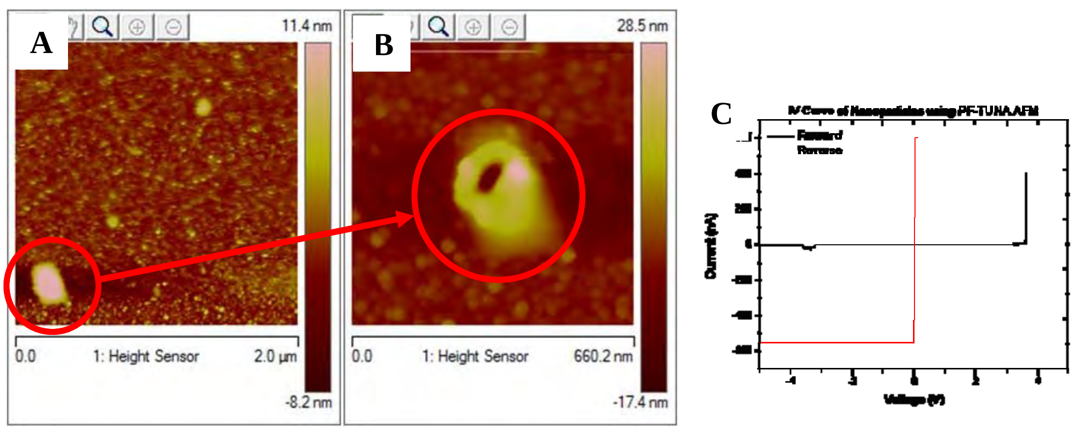

Figure 2: Tapping mode AFM scans A) before electrical biasing and B) after electrical biasing. C) Shows corresponding forward (-5V → 5V) and reverse (5V → -5V) IV sweeps of biasing the nanoparticles.

After unsuccessfully attempting to measure memristive properties of individual nanoparticles, we moved to integrating nanoparticles into nanoscale "via" devices. In this approach, nanoparticles were spread on silicon wafers with nanoscale vias (holes) etched into them. The excess particles were swept off of the surface, leaving only nanoparticles in vias. These nanoparticle filled vias were then capped with top electrodes by direct capping with electron beam induced deposition (EBID). These nanoscale aggregates of nanoparticles were then measured using a cAFM, which also yielded diode-like and limited switching behavior.

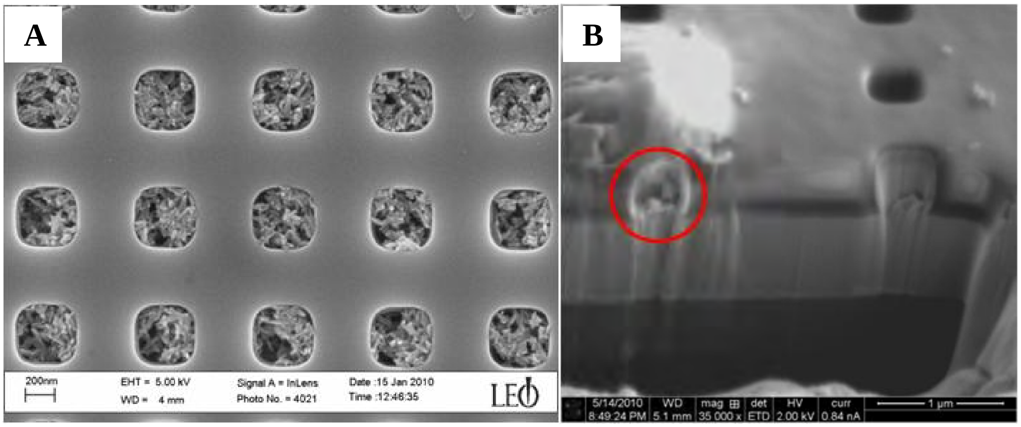

Figure 3: Nanoscale vias filled with TiO2 nanoparticles imaged A) top down before Pt capping and B) cross section of filled via after Pt capping.

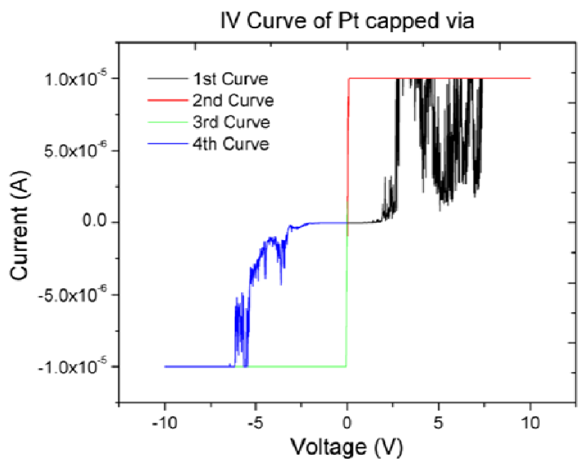

Figure 4: Current-voltage (IV) curve using cAFM of a filled nanoscale via with TiO_2 nanoparticles capped with EBID Pt.

At the conclusion of this phase of the effort, we determined that individual nanoparticles were highly difficult to measure electrically and that neither individual particles or small aggregates of particles could be switched memristively, using the available characterization methods in our laboratory. We therefore moved to a hybrid approach, of loading insulating films with nanoparticles for memristive devices.

4.4 Integration of nanomaterials into thin films for memristive devices

After unsuccessfully fabricating memristive devices from individual nanoparticles or small aggregates of nanoparticles, we focused on incorporation of nanoparticles into insulating thin films, to yield tunable memrsitive devices. We utilized an insulating spin-on glass (SOG) material, hydrogen silsesquioxane (HSQ). This material can be spun onto silicon wafers, yielding uniform thin films. We mixed titanium oxide, hafnium oxide, and silicon oxide nanoparticles with HSQ and spun the blended material onto metal-coated silicon oxide wafers to yield metal/insulator devices. Top contacts were formed on these devices using a shadow mask/evaporation technique. Devices were then probed with a standard semiconductor probe station. This approach yielded switchable devices that behaved as memristors (having a range of unipolar, bipolar, or non-polar behavior). Our results showed that the V_{on} and V_{off} of resulting devices was not affected by the presence of metal oxide nanoparticles, but that the R_{off} / R_{on} was affected. In fact, the R_{off} values were highly affected by the presence of nanoparticles as shown in Figure 5 below.

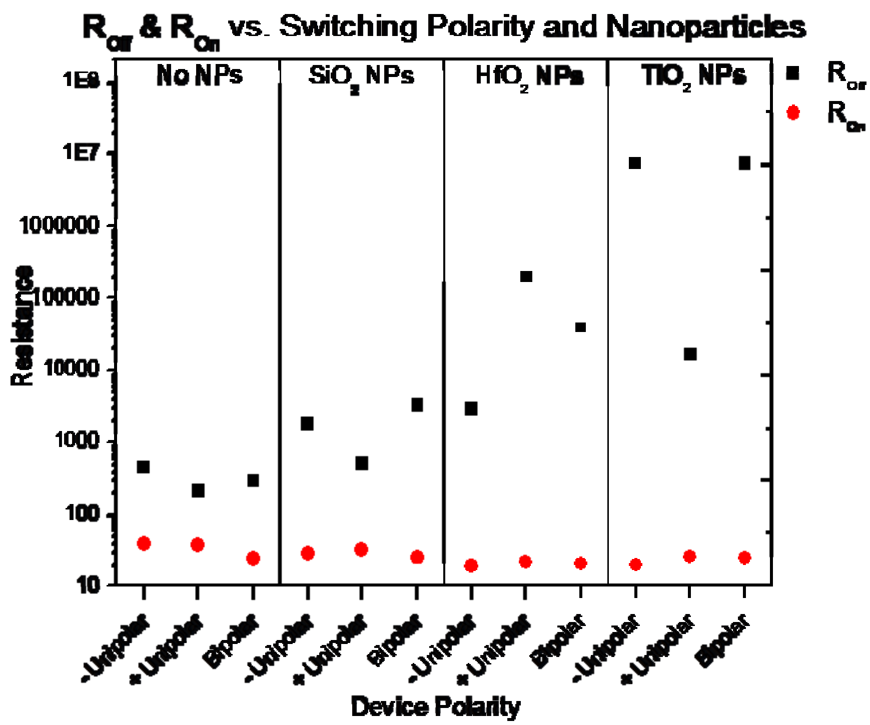

Figure 5: R_{Off} & R_{On} as a function of switching polarity and presence of nanoparticles (SiO_2, HfO_2, and TiO_2) in HSQ films.

These results demonstrate that memristive devices can be fabricated using nanoparticle-loaded thin films, and that the memristive properties of these devices are tunable, based upon the nanoparticle composition and size. These devices are far simpler to fabricate than traditional thin-film based devices, and may have applications for follow-on efforts in memristive device development.

4.5 Publications in This Project

- Rice, Zachary; Bergkvist, M; Cady, N. (2009, December). Terminal Phosphate Group Influence on DNA-TiO2 Nanoparticles Interactions, *Proceedings of the Materials Research Society (MRS)*, Boston, MA.

- N.C. Cady, M. Bergkvist, N.M. Fahrenkopf, P.Z. Rice, J.E. Van Nostrand (2010, June). Biologically self-assembled memristive circuit elements, *Proceedings of the ISCAS*, Paris, France.

- J.E. Van Nostrand, R. Cortez, Z.P. Rice, N.C. Cady, and M. Bergkvist. Morphology, Microstructure and Transport Properties of ZnO Decorated SiO2 Nanoparticles. (2010) *Nanotechnology.* 21 415602.

- Rice, Zachary; M. Bergkvist, J.E. Van Nostrand, N. Cady (2010, November). Titanium Dioxide Nanoparticles for Memristive Nanoelectronics, Materials Research Society (MRS), Boston, MA.

- N. Fahrenkopf, P.Z. Rice, N.C. Cady. Nucleic acid based biosensing. In: *Nanobiomaterial Handbook.* Balaji Sitharaman, Ed., 2011. CRC Press.

5. Conclusions

This effort showed that memristive switching of individual nanoparticles is highly difficult to measure, and that individual particles may not, indeed, be resistively switched. However, the effort yielded synthesis methods for tuning nanoparticle size, composition, and crystallinity, which will be a useful starting point for other nanoparticle-based efforts. In addition, we were able to incorporate metal oxide nanoparticles into insulating thin films, which did have memristive switching characteristics. Further, the composition and size of the particles had an effect on switching behavior, which could be used to tune the switching dynamics of memristors in more complex electrical devices. We see this as an exciting approach towards “dialing in” the electrical properties of memristors.

6. References

[1] D. B. Strukov; G. S. Snider; D. R. Stewart; R. S. Williams "The missing memristor found" *Nature*, 453(7191): 80-83 (2008).

List of Acronyms

XRD: X-ray diffraction

cAFM: Conductive atomic force microscopy

TEM: Transmission electron microscopy

EBID: Electron beam induced deposition

DLS: Dynamic light scattering