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14. ABSTRACT

A piezo-force microscope (PFM) system was acquired under this support for characterization of flexoelectric micro/nanostructures in a controlled environment. The system was installed successfully and a few graduate students were trained by the vendor. Both piezoelectric samples and flexoelectric samples were prepared and characterized using this new system.

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PFM, Flexoelectricity, Flexoelectric characterization

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Report Title

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ABSTRACT

A piezo-force microscope (PFM) system was acquired under this support for characterization of flexoelectric micro/nanostructures in a controlled environment. The system was installed successfully and a few graduate students were trained by the vendor. Both piezoelectric samples and flexoelectric samples were prepared and characterized using this new system.

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

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

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

TOTAL:

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

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

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

TOTAL:

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

(d) Manuscripts

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

TOTAL:

Number of Manuscripts:

Books

Received   Book

    TOTAL:

Received   Book Chapter

    TOTAL:

Patents Submitted

Patents Awarded

Awards

Dr. Jiang won the 2015 Outstanding Researcher Award of Department of Mechanical and Aerospace Engineering at NC State.

Dr. Jiang won the 2015 Chancellor Innovation Funding award at NC State.

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

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

DURIP: Piezoresponse Force Microscope (PFM) with Controlled Environment for Characterization of Flexoelectric Nanostructures

Final Report (W911NF-13-1-0253)
(For period 8/01/2013-1/31/2015)

Wenbin Huang and Xiaoning Jiang

Department of Mechanical and Aerospace Engineering
North Carolina State University
Raleigh, NC 27695

Submitted to

Dr. William Clark
Army Research Office

April 21, 2015

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4. Statement of the problem

Multimodal sensing for detection, identification, and discrimination of battlefield environments, including enemy and friendly elements and their activities is critical to achieving army missions. Novel seismic sensors, acoustic sensors, electromagnetic sensors and infrared (IR) detectors are among in-need multimodal sensing of vehicles, personnel, weapons, projectiles, explosives, landmines, IEDs, and motion.

At present, piezoelectric materials and structures are used extensively for the above sensors and detectors largely due to the fact that the nature of piezoelectricity renders both active and passive sensing with fast response, low profile and low power consumption. Acoustic and seismic sensors are used to ascertain the exact target location, speed, direction of motion, and classification on the basis of their acoustic signatures for ground-based, aerial, and naval battlefield applications [1, 2]. Acoustic sensors are hard to be fooled by countermeasures since many targets cannot operate without generating a detectable acoustic and seismic signature. Piezoelectric sensors offer several advantages over other types given that they are self-generating transducers exhibiting relatively high sensitivity, low noise and low cutoff frequency [2]. However, countermeasures with noise reduction could minimize the acoustic signal level, which is a challenge in terms of sensitivity and bandwidth of existing acoustic sensors. For IR detection, a recent report on competitive technologies of third generation infrared photon detectors disclosed that the main limitations for the state-of-the-art IR detection technologies came from sensing read out circuits [3]. Uncooled IR detectors with piezoelectric read out circuits showed improved sensitivity [4]. Piezoelectric acoustic resonators also demonstrated unprecedented temperature sensitivity for IR detection [5]. For electromagnetic sensors, recently discovered magnetoelectric structures (combined magnetostrictive and piezoelectric structures) showed potential for detection of extremely weak magnetic fields [6]. It can be concluded that piezoelectric materials and structures have played an unparalleled role in these mission-critical multimode sensors and detectors. Conventional lead based piezoelectric materials are dominant in the present piezoelectric sensors and detectors, but the figure of merit property (electrical power density or the product of the piezoelectric coefficient and the voltage coefficient) of these piezoelectric materials and sensing structures are being challenged by the increasingly harsh battlefield needs [2], let alone the fact that lead based piezo materials are not environmentally friendly if a large amount of sensors is deployed and unattended. Furthermore, miniaturization of multimodal sensing becomes inevitable as more functions must be integrated in a system fulfilling complex tasks. However, *miniaturization in piezoelectrics has found that the figure of merit property of piezoelectric materials and sensing structures decrease as piezoelectric structures are scaled down.* Examples include thin films showing significantly reduced piezoelectric properties [7]. A similar observation has been found with piezoelectric nanostructures [8], though elastic properties of piezoelectric structures were found increased at nano scale. In order to further advance miniaturized multimodal sensing technology, innovation in piezoelectric materials and structures must take

place to address the increasing challenges in the aspects such as sensitivity, bandwidth, miniaturization, power supply and communication to address future battlefield needs.

In addition to piezoelectric materials, a broad range of smart sensing materials and structures including pyroelectric materials, electrostrictive materials, magnetostrictive materials, magnetoelectric materials, flexoelectric materials, etc. form the foundation of multimodal sensing technology. These smart materials fall in the family of dielectric and ferroelectric materials, and they share the similar core electric-mechanical characterization technique. *The characterization of these materials and structure systems for multi-spectrum properties becomes critically important to advance multimodal sensing technology.* The piezo force microscope system (PFM) was hence proposed under the DURIP program for the above mentioned characterizations.

5. Summary of the results

5.1 List of equipment in the PFM system

The PFM system acquired under this grant consists of the following units: a Brucker Nano AFM system [9], environment control unit (temperature, gas/liquid, vacuum, and vibration/acoustic isolation), and electronics and display units. Key components are listed in Table 1. In addition to key AFM specifications this PFM will retain, specifications related to piezoelectric/flexoelectric characterizations include: minimum displacement can be measured is less than 0.03nm; force range pN- μN; minimum current can be measured will be less than 30-40 fA; temperature range -30ºC- 150 ºC, which covers the need for most flexoelectric characterizations; chamber medium includes gas and liquid; cantilever vibration frequency Hz-MHz. With this PFM, the following new characterizations of *flexoelectric nanostructures* can be performed, including piezoelectric coefficient measurement, dielectric properties measurement, flexoelectric coefficients measurement, and mechanical properties measurement.

Table 1: List of the purchased equipment under the grant

Category	Items	Manufacturer/Vendor	Cost
PFM system		Brucker Nano, Inc., Santa Barbara, CA	$166,626
	Bruker Nano AFM (Dimension Icon)		
	AR RF power amplifier 10KHZ-250 MHZ	Amplifier Research Corp., Souderton, PA	$9,785
Materials/Supplies/Services	4284A Agilent LCR meter	Paragon, Bolton, MA (refurbished)	$4,999

	Across International AccuTemp-09fr thermal oven with accessories	Across International, Livington, NJ	$2,571.55
	Thorlabs NRT100 motorized linear stage	Thorlabs, Inc., Newton, NJ	$1,960
	Bruel and Kjaer 2706 power amplifier	ValueTronics, Elgin, IL (Refurbished)	$1,350
	Gas cylinder and other materials, supplies and services	Fisher Sci., Ellsworth Adhesives, etc.	$4,496.76
Indirect	Indirect cost of materials, supplies and services	NC State	$7,957
Total			$199,707.62

5.2 Summary of research projects involving the usage of above equipment

The following two grants benefited directly from the PFM system acquired. More research tasks taking advantage of this tool are being carried out at PI's group.

- "Flexoelectricity in Nanostructures: Theory, Nanofabrication and Characterization", W911NF-11-1-0516, funded by DOD DA Army Research Office.
- "Flexoelectric Strain Gradient Sensors- a New Sensing Technology for In-situ Structure Health Monitoring", CMMI-1068345, funded by National Science Foundation.

Due to scale effect, flexoelectric nanostructures have great potential as novel type of electromechanical devices. To investigate the flexoelectric properties of the ferroelectric nanostructures, piezo force microscope is needed to apply large strain gradient in miniaturized area and monitor the electrical response simultaneously. On the other side, understanding of the flexoelectric property of the bulk material is important for predicting and validating the enhanced performance of the flexoelectric nanostructures. Purchased equipment, together with our previously possessed tools, form a system to enable the preparation and systematical characterization of the flexoelectric structures at varied dimensions. The usages of the above equipment are simply summarized as following:

The LCR meter and electrometer can be used for measuring the dielectric properties of the flexoelectric materials, which is supposed to have a direct linear effect upon the flexoelectric coefficient.

Vacuum oven assists to provide a controllable temperature environment for the material characterization. This is in great need because of the sensitive reliance of dielectric properties on the temperature. Moreover, vacuum oven plays a big role in the nanostructure preparation process.

The flexoelectric coefficient can be evaluated by a linear motorized stage based system powered by a power amplifier. The whole characterization system needs be placed in the oven for the coefficient measurements, thus a remote controllable actuating part (the motorized linear stage) is required. In addition, the linear stage can be coupled with the PFM system to offer another DOF control ability. For example, the pre-strain or stress can be applied to the sample by the linear stage. This capability allows the PFM to monitor the strain effect on flexoelectric properties.

Initial results obtained by PFM

A. *Flexoelectric nanostructure characterization*: PFM has been employed to characterize a nano pyramid structures on $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) thin film fabricated using focused ion beam technique. Figure 4 illustrates the cross section profiles of two BST nano pyramid structures with the bottom diameter of 8 µm and 2 µm, respectively. To study the flexoelectric property, a cyclic load was applied upon the pyramid surface through the conductive AFM tip. The tip was maintained in contact with the pyramid hence the generated current could flow into the electric circuit built in the PFM system thus being measured. A typical tip deflection waveform is plotted in Figure 5, together with the measured flexoelectric current output. Based on this mechanism empowered by the PFM system, the flexoelectric nanostructures can be characterized effortless. More study is been performed and a journal paper submission can be expected in 2015.
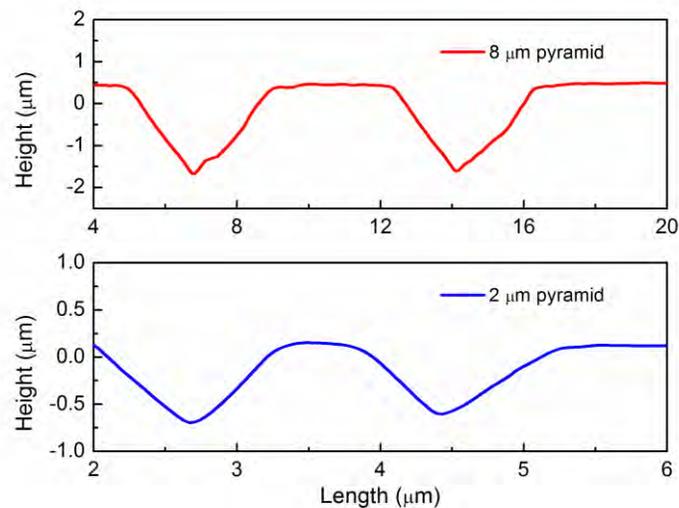

Figure 4. The one dimensional AFM profiles of two nano pyramids with different sizes.
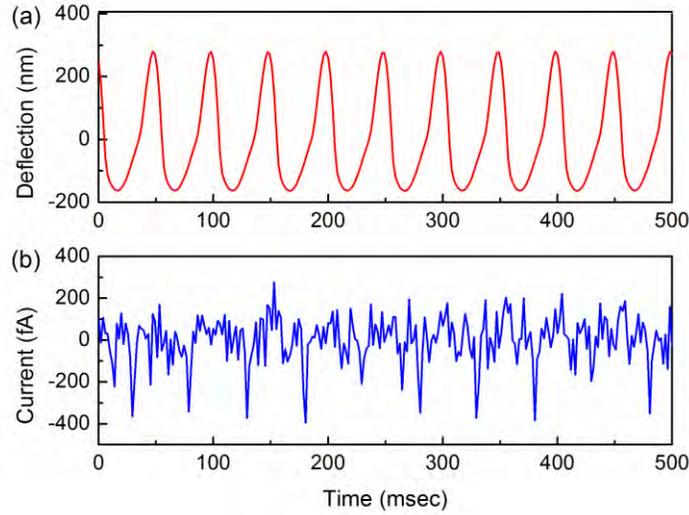
Figure 5. (a) Real time deflection of the PFM probe. (b) Current reading from the pyramid area under 760 nN loading.

B. *Piezoelectric nano-characterization*: Electrical domain structure plays a significant role in the performance of piezoelectric materials. Miniaturized domain size (nano scale) and regularly oriented domain configuration lead to higher piezoelectric coefficient. Using interference lithography technique, we developed a nano grating composite electrode on a PMN-PT single crystal. It comprises a manganese oxide nano grating structure covered by a blanket gold layer. The surface was scanned by the AFM as shown in Figure 6. The pitch is about 200 nm and the kerf between manganese oxide gratings is 50 nm. Electrical poling across the wafer could generate nano domain structure along the thickness direction. Imaging of the piezoelectric domains underneath the electrode using PFM is under way. The in-plane and out-of-plane piezoelectric response will be studied. A journal paper can be prepared after the study is completed.
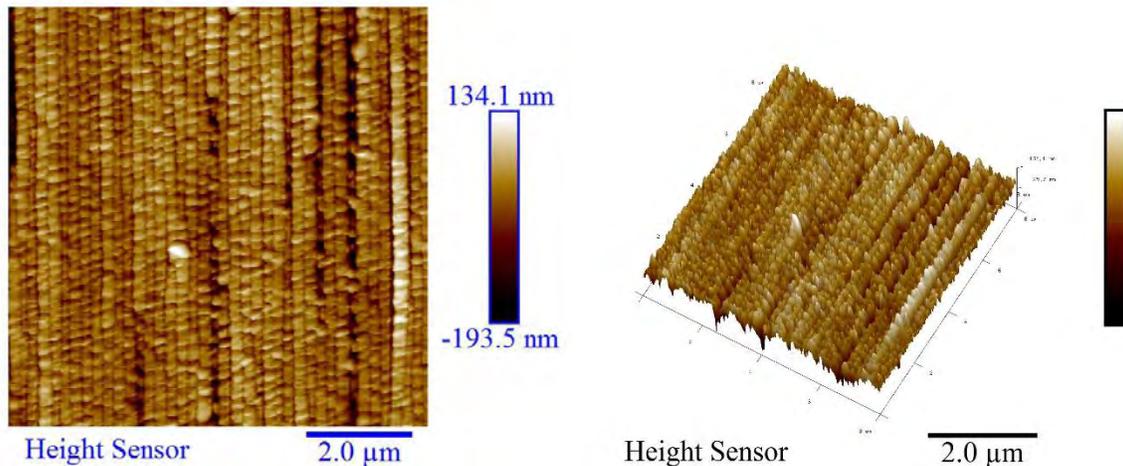

Figure 6. Profile of the nano grating electrode on PMN-PT single crystal.

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C. Roughness measurement: we recently demonstrated a novel optoacoustic transducer by using candle-soot particles CSPs-PDMS composite. The morphology and structure of candle soot nanoparticles (CSPs) and PDMS composite can be observed in Figure 4. The thickness of CSPs + PDMS and PDMS layer is 5.99 ± 0.5 μm and 18.44 ± 1.3 μm, respectively. It is more clearly to indicate that CSPs is embedded and wrapped with thin PDMS layer as shown in Figure 4(b) and (c). The surface roughness of CSPs was measured by a canning probe microscopy (Dimension icon, Bruker, Santa Barbara, CA), and the root-mean-square (RMS) surface roughness of CSPs is about 200 nm. It is confirmed that candle soot nanoparticles can provide an efficient light absorption and heat transfer performance. With the excitation using a low laser energy density (1.94 mJ/cm^2), the CSPs-PDMS composite laser transducer showed a high energy conversion coefficient (1.68×10^{-3}) and acoustic pressure amplitude (1.88 MPa) at a broad frequency range (21 MHz) among the transducers using carbon black CB-PDMS composite, carbon nanofibers CNFs-PDMS composite and CSPs- PDMS composite. A journal manuscript is being prepared.
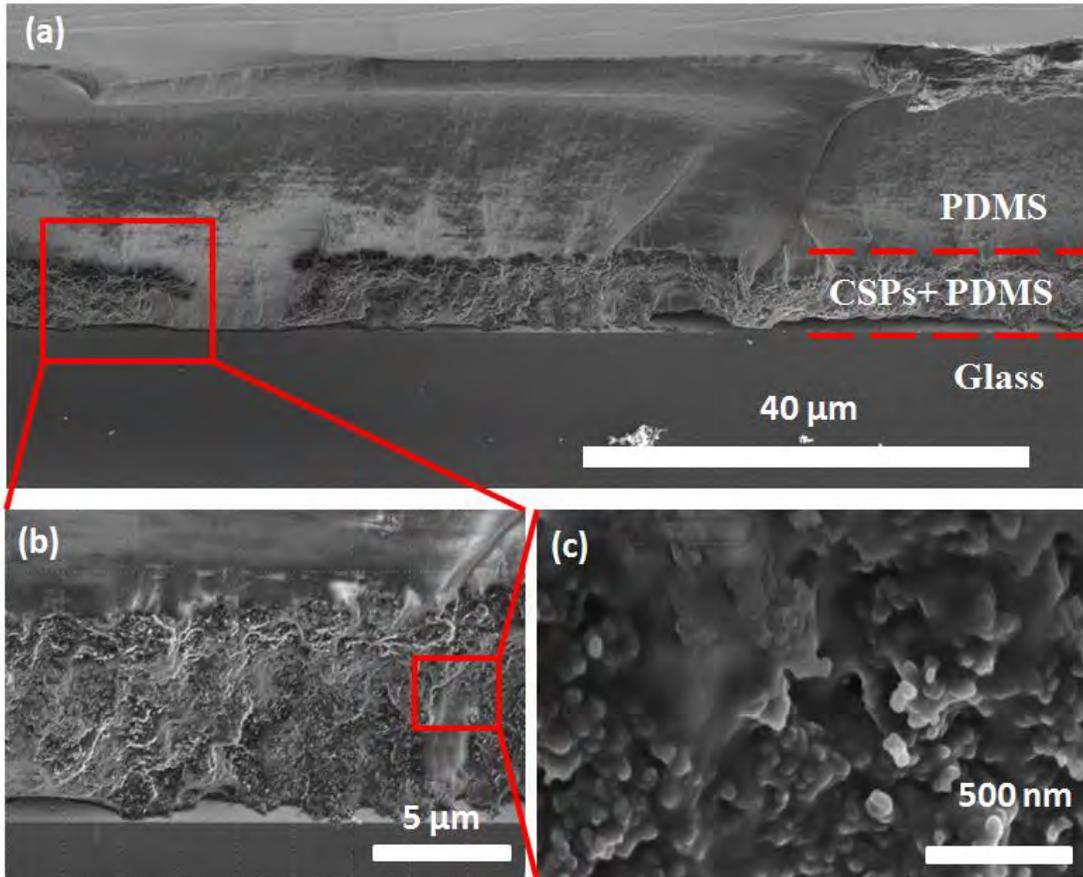

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5.3 Summary

The acquired PFM system provides unprecedented characterization capabilities for research on advanced flexoelectric sensing materials and nanostructures. Extensive understanding of multispectral properties of sensing materials and nanostructures will indeed facilitate the research and development of multimodal sensing technology, and research-related education.

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