

# NANOscientific

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The Magazine for Nanotechnology

## SMART ON-DEMAND SELF DEFENSIVE COATINGS OF BIOMEDICAL DEVICES HOW SELF ACTIVATING ANTI BIOTICS WORK

p. 6

## GREEN TECHNIQUE DEVELOPING ENERGY FROM NATURAL WOOD WITHOUT CORROSIVE CHEMICALS

p. 13

## USING SCANNING KELVIN PROBE MICROSCOPY TO ANALYZE ELECTRICAL PROPERTIES OF METAL, SEMICONDUCTOR DEVICE SURFACES, ORGANIC AND BIOLOGICAL MATERIALS

p. 19

## HOW PIEZORESPONSE FORCE MICROSCOPY IS USED TO OBSERVE LOCAL ELECTROMECHANICAL RESPONSES AT NANOMETER

p. 9





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# TABLE OF CONTENTS

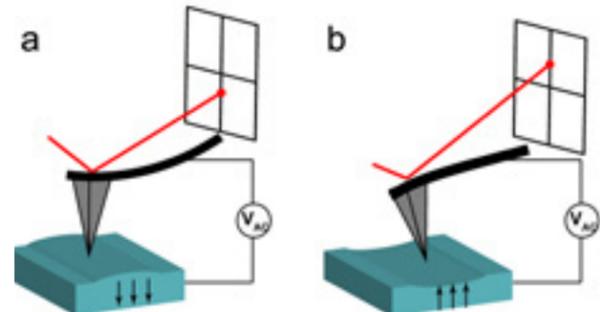
Nano-Scientific Fall 2017

**Feature Article: “Smart on-demand Self Defensive Coatings of Biomedical Devices - How Self Activating Anti Biotics Work”** Feature Interview with Dr. Svetlana Sukhishvili, Professor, Department of Materials Science and Engineering Texas A&M University 5



p. 6

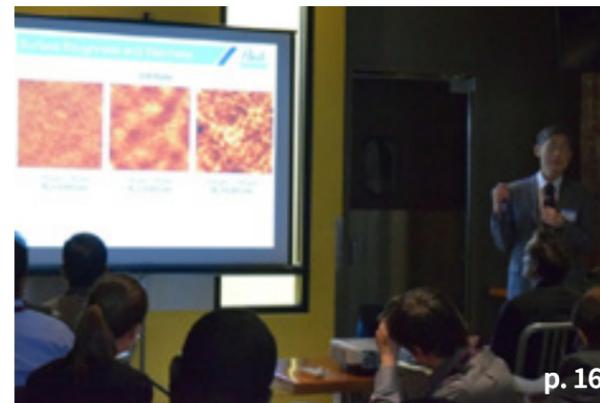
**Application Note: Using Piezoresponse Force Microscopy to Observe Local Electromechanical Responses at Nanometer:** PFM, also termed dynamic-contact electrostatic force microscopy (DC-EFM) by Park Systems, is performed in an atomic force microscope (AFM) operating in contact mode with an electrically-biased conductive tip to probe local nanoscale displacements in response to electronic stimuli 7



p. 9

**Feature Story: Developing Energy from Natural Wood Without Corrosive Chemicals** High surface area mesoporous carbon is successfully manufactured from natural wood via this green technique under development at Intelligent Composites Laboratory, The University of Akron – Feature Interview with Jiahua Jack Zhu, Assistant Professor, Chemical & Biomolecular Engineering 13

**Feature Interview: Park Systems AFM Luncheon at Semicon West Draws Standing Room Only Crowd** Presentations by Dr. Sang-il Park, CEO and Founder of Park Systems & Prof. Krishna Saraswat Department of Electrical Engineering Stanford University 16



p. 16

**Application Note: Using SKPM with Park AFM to analyze electrical properties of metal, semiconductor device surfaces, organic and biological materials** 19

**In the News: Park Recognizes AFM Scholarship 2017 Awardees** 23

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INSET PHOTO ON COVER: 3D representation of multilayer ceramic capacitor (MLCC) as characterized by piezoelectric force microscopy (PFM). Topography (height) data with PFM phase data overlay. Scan size: 7 μm x 7 μm. This image of a multilayer ceramic capacitor (MLCC) sample was acquired using piezoelectric force microscopy (PFM) wherein the topography (height) data has been overlaid with PFM phase data. Elevated features on the sample surface lack clear PFM phase signals which suggest they do not exhibit piezoelectric behavior. Furthermore, it stands to reason that areas which are not observed to have piezoelectric properties are most likely to be composed of metal electrode. Areas in between the elevated areas do exhibit PFM phase data and are therefore believed to be composed of ceramic dielectric, the piezoelectric material in the capacitor design. Within the ceramic dielectric, we can also observe areas of bright and dark contrast which indicate a different polarization vector direction. The absolute direction of the vector (and the color of these regions) will vary due to user settings such as the polarity of the bias applied to the sample. Lastly, it is also important to note that several of the elevated rows of metal electrode have gaps where ceramic dielectric material is passing through. These gaps could potentially lead to reduced capacitor performance or outright device failure.



Keibock Lee,  
Editor-in-Chief

## MESSAGE FROM EDITOR

The global market for nanotechnology products is expected to reach about \$64.2 billion by 2019 and nanotechnology now impacts almost every industry sector. From changing the way medicine and diagnostic procedures are given to developing new and efficient ways to generate electricity, nanotechnology continues to transform the world in many ways to further benefit society.

How do scientists see what's going on in the extremely small world of nanotechnology? Better microscopes are instrumental in nanotechnology developments and today's nano scientists use high-powered microscopes with unique methods to see surface features at the atomic scale including microscopes that use thermal, magnetic, capacitive and electrochemical properties.

In this issue, we showcase one of the new revolutionary medical devices poised to improve medical technology in a feature interview with Prof. Svetlana Sukhishvili from Texas A&M University. Her research in stimuli-responsive polymers has uncovered “Smart on-demand Self Defensive Coatings”, highly effective for release of anti biotics in the human body.

We also feature an example of a newly patented way to produce clean energy from Natural Wood without corrosive chemicals in a feature story highlighting the research at the Intelligent Composites Laboratory at The University of Akron.

Semiconductor devices continue to advance along the technology progression with newer materials and device structures. Nanoscale microscopy plays a key role in advancing this new

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technology. This issue also features interviews with Dr. Sang-il Park, CEO and founder of Park Systems about the role of AFM and from Dr. Krishna Saraswat from Stanford University about some of the potential future innovations in interconnects.

We also recognize two of the latest awardees of the Park AFM Scholarship which also provides access to a Park AFM to support their research. Park AFM scholarships are giving financial incentive to pioneering new researchers in Nanotechnology at leading academic institutions world-wide.

We also feature application articles on the latest ways to use AFM that includes Piezoresponse Force Microscopy in multi layered ceramic capacitor and using SKPM with Park AFM to analyze electrical properties.

Our mission at Nano-Scientific is to publish informative articles about the many advances in nano Science and the new microscopy methods that are enabling the evolution of new nano technology across so many sectors of the economy.

We are in our third year of production and we invite you to subscribe to receive our future issues and please submit your story ideas; we would love to publish information about YOUR research!

## OHIO STATE UNIVERSITY DEVELOPS REGENERATIVE MEDICINE BREAKTHROUGH CALLED TISSUE NANOTRANSFECTION USING NANOTECHNOLOGY CHIP

Photo Caption: Researchers at The Ohio State University Wexner Medical Center have developed a device that can switch cell function to rescue failing body functions with a single touch. The technology, known as Tissue Nanotransfection (TNT), injects genetic code into skin cells, turning those skin cells into other types of cells required for treating diseased conditions. In laboratory tests, this process was able to heal the badly injured legs of mice in just three weeks with a single touch of this chip. The technology works by converting normal skin cells into vascular cells, which helped heal the wounds.

nano-scientific 5



## DR. SVETLANA SUKHISHVILI PROFESSOR, DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING TEXAS A&M UNIVERSITY

### What are smart self-defensive anti-biotic coatings and how were they discovered?

The practical problem we address is bacterial infection associated with biomaterials, such as orthopedic implants or urinal devices, for example. The traditional treatment of biomaterial-associated infections with systemic antibiotics is often inefficient because of the formation of bacterial biofilms in which bacteria are poorly responsive to treatment. Polymer coatings have been earlier explored to prevent surfaces from colonization with bacteria, but in most cases these coatings continuously elute antibiotics, increasing emergence of antibiotic resistance.

Our focus is on another approach, which minimizes the emergence of antibacterial resistance. We are using smart coatings, which contain antibiotic, but do not elute it until they get activated by stimuli. Prior work explored such on-demand activation of polymer coatings when various external stimuli, such as pH, temperature or light are used. In contrast, our group explores a different type of the coatings - "self-defensive" coatings - which are triggered by bacteria rather than external stimuli. Specifically, we are using acids excreted by bacteria as triggers for antimicrobial release from the coating to combat adhering bacterial. By applying confocal imaging techniques, we have demonstrated that bacterial acidification can be highly localized even in buffered physiological conditions, and that this highly

localized bacterial signals can be used to release antimicrobial cargo from the films and kill adhering bacteria.

### How do layer-by-layer films enable the self activation process?

We work with ultra-thin layer-by-layer films, which are built when molecules of at least two types are layered at surfaces in a simple dip-, spray- or spin, aqueous-based deposition. The molecules are held together in the coating by through electrostatic pairing or and hydrogen bonding interactions. One type of these molecules can be an antibacterial compound.

When these films are assembled, electrostatic interactions are balanced and the film interior is overall electrostatically neutral. Such coatings are stable and do not release antimicrobials at a constant pH, i.e. in absence of bacteria. When a signal - i.e. bacteria-induced acidification - is 'felt' by the coatings, the balance of charges shifts and the coating releases antibiotic to compensate for the bacteria-induced charge misbalance.

### What is the Role of 3D Hierarchical Nanostructures for this process?

Building hierarchical nanostructures at solid surfaces (such as on titanium, often used as an implant material) boosts the efficiency of the self-defensive coatings. Here, an antibacterial layer-by-layer (LbL) film and hierarchical nanotopography act synergistically to efficiently

*Pictured: Prof. Svetlana A. Sukhishvili (front row) with her research group at the Department of Materials Science and Engineering Texas A&M University where their research focuses on many areas of polymer science including stimuli-responsive all-polymer and polymer nanocomposite assemblies for sensing, separation and biomedical applications.*

**“OUR GROUP EXPLORES A DIFFERENT TYPE OF THE COATINGS - “SELF-DEFENSIVE” COATINGS - WHICH ARE TRIGGERED BY BACTERIA RATHER THAN EXTERNAL STIMULI. SPECIFICALLY, WE ARE USING ACIDS EXCRETED BY BACTERIA AS TRIGGERS FOR ANTIMICROBIAL RELEASE FROM THE COATING TO COMBAT ADHERING BACTERIAL.”**

**- DR. SVETLANA SUKHISHVILI, PROFESSOR, DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING TEXAS A&M UNIVERSITY**

## FEATURE INTERVIEW

# SMART ON-DEMAND SELF DEFENSIVE COATINGS OF BIOMEDICAL DEVICES - HOW SELF ACTIVATING ANTIBIOTICS WORK

antibiotics and kill bacteria. This occurs in a couple of different ways: (a) first, the overall increase in the surface area leads to a greater exposure of bacteria to antibiotic coatings; (b) when bacteria land on the 3D-nanopillared structures, bacterial adhesion is reduced and their susceptibility to antibiotics is increased.

### How is Atomic Force Microscope used in your research and why is it helpful?

AFM is a working horse in our explorations of smart coatings. One type of these coatings contains assembled block copolymer micelles, whose cores controllably swell /deswell in response to changes in environmental pH or temperature. In this case, we find AFM that is performed in liquid environment (in water) to be indispensable to directly observe expansion and contraction of LbL-assembled spherical micelles in response to various stimuli.

### How do you collaborate with The Spallation Neutron Source at ORNL? Is this type of collaboration with other researchers important and beneficial to your work?

To study the functionality of our smart layer-by-layer coatings, we need to understand their internal structure and dynamics of assembled molecules. To that end, graduate students in our group closely collaborate with John Ankner from SNS ORNL to design and perform experiments that enable such an understanding. We create nanoscopically structured films at the surface of silicon substrates, while assembling some deuterated components in order to be able to detect film structure using neutron

reflectometry (NR). Students from my group then travel to ORNL to perform NR experiments. The collaboration has been extremely productive, resulting in almost a dozen joint publications with SNS ORNL within the last 10 years. We hold weekly conference calls with John Ankner to discuss prior results and plan new experiments. These interactions are mutually beneficial and enjoyable. Graduate students greatly enrich their experiences by working with the national lab experts, while through both personal interactions and through participation in the SNS Users Workshops we have a unique opportunity to provide feedback on instrumental development at ORNL and interact with ORNL computational/modelling community.

### What nanotechnology advances do you see in the future for biomedical devices?

While many of the technologies we are working on still wait to make their way to the market, I envision that the work of the highly inventive scientists in the area of smart coatings will eventually make a tremendous impact on the future of biomedical devices. The coatings, which are nanoscopically thin, and/or are deposited on nanostructured substrates can be designed to be extremely effective against bacterial adhesion and biofilm formation. The 'lack' in their thickness can be compensated by the smart design that assures targeted, on-demand 'activation' to deliver antimicrobials. In the future such innovative design will assure that the coatings will be available to completely eliminate chances of infection of biomedical devices, while the side effects and the development of antibiotic resistance associated with the use of these devices will be minimized.



Professor Sukhishvili is currently a Professor at Texas A & M University Department of Materials Science and Engineering where her research group focuses on stimuli-responsive all-polymer and polymer nanocomposite assemblies for sensing, separation and biomedical applications, structure and dynamics of polyelectrolyte assemblies, materials with controllable optical, swelling and drug-release responses, remote manipulation of material shape, smart antibacterial materials and surface modification for controlling wettability, adhesion and adsorption. She received a B.S. in Polymer Science with an award for excellence, Moscow State University, Russia and Ph.D. in Polymer Chemistry, Moscow State University, Russia. She has served as a professor at University of Illinois, MIT, Stevens Institute Technology, Moscow State University where she has taught courses in Polymer Science, Biomaterials and Biophysical Chemistry and Nanoscience.

Prof. Sukhishvili is the recipient of numerous awards including Provost's Entrepreneurship Award, NSF Special Creativity Award, Davis Award for Research Excellence, Award for Distinguished Scientific Achievement American Coatings Association and is a member of the Editorial Advisory Board for Particle & Particle Systems Characterization and is a frequent guest presenter at American Chemical Society and American Physical Society and other industry events.



Prof. Sukhishvili is a Member of the Executive Committee of the new Soft Matter Research User Facility at the Department of Materials Science & Engineering at Texas A&M

**“WE FIND AFM THAT IS PERFORMED IN LIQUID ENVIRONMENT (IN WATER) TO BE INDISPENSABLE TO DIRECTLY OBSERVE EXPANSION AND CONTRACTION OF LBL-ASSEMBLED SPHERICAL MICELLES IN RESPONSE TO VARIOUS STIMULI.”**

**“We want this facility to become an interdisciplinary research center,” said Dr. Svetlana Sukhishvili, Professor of Materials Science and Engineering and a member of the facility’s executive committee. “The faculty will facilitate targeted faculty hires in this discipline in many colleges. It will be a premiere location to show our students and visitors the exciting discoveries we are making and hopefully encourage them to join our efforts.”**

The facility will help users conduct research to improve multifunctional polymer-based materials that are used in many applications, including energy, health care and transportation, among others, and will benefit the entire Texas A&M research community. The project includes 29 faculty members across multiple colleges and centers, including the colleges of engineering, science, and agriculture and life sciences at Texas A&M, in addition to the Texas A&M Health Science Center, representing all entities across the university actively involved in soft materials-related research and is the only

user facility in Texas specifically dedicated to the characterization of multifunctional soft materials.

Sukhishvili and the members of the executive committee are hopeful that collaborative efforts in this facility will enable new discoveries in health care, soft robotics, biomanufacturing and environmental protection by acting as a nucleus of activity for collaborative research efforts not only at Texas A&M, but ideally across the state and nation. The soft matter facility is funded through the Research Development Fund for about \$1.7



Texas A & M University with a current enrollment of over 60,000 was founded in 1876 as the state’s first public institution of higher learning and is one of only 17 institutions in the nation to hold the triple designation as a land-grant, sea-grant, and space-grant university. Texas A&M stands today as one of the largest research universities in the United States with faculty-researchers generating more than \$866 million in research expenditures, all while enhancing undergraduate and graduate education by providing hands-on research.

**“AFM IS A WORKING HORSE IN OUR EXPLORATIONS OF SMART COATINGS.”**

# USING PIEZORESPONSE FORCE MICROSCOPY TO OBSERVE LOCAL ELECTROMECHANICAL RESPONSES AT NANOMETER:

**CHRISTINA NEWCOMB, GERALD PASCUAL, BYONG KIM, AND KEIBOCK LEE PARK SYSTEMS INC.**



**APPLICATION NOTE #19**

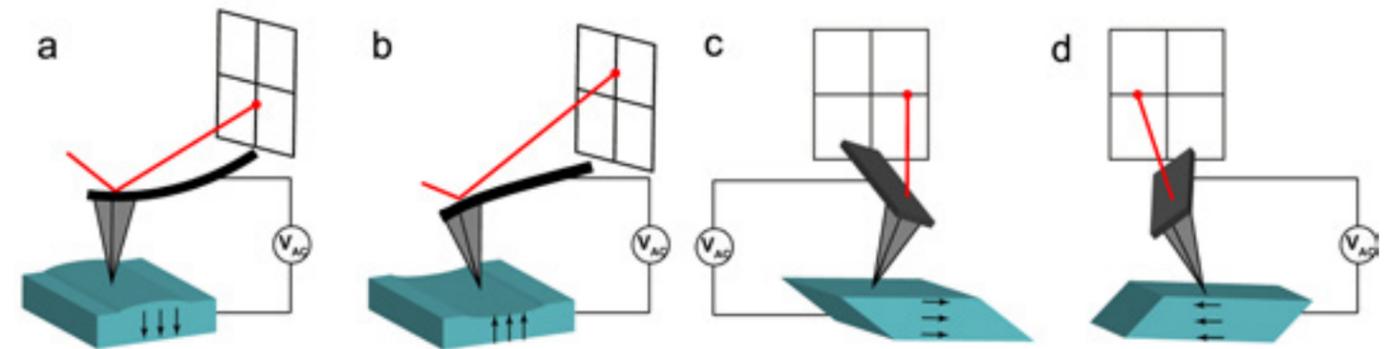


Figure 1. A schematic representation of (a-b) vertical and (c-d) lateral PFM. The AFM laser shows vertical deflections which correspond with (a) downward or (b) upward out-of-plane electrical polarization. In lateral PFM, the cantilever will exhibit torsion in response to (c-d) lateral in-plane polarization directions. Black arrows indicate the direction of polarization vector in each case assuming that the relationship between polarization and crystal orientation is conserved.

THE COUPLING BETWEEN AN ELECTRICAL AND MECHANICAL RESPONSE IN A MATERIAL PROPERTY CAN BE FOUND IN A VARIETY OF APPLICATIONS RANGING FROM SENSORS AND ACTUATORS TO ENERGY HARVESTING AND BIOLOGY. THIS PROPERTY CAN BE DIRECTLY MEASURED USING PIEZORESPONSE FORCE MICROSCOPY (PFM) IN PARK SYSTEMS ATOMIC FORCE MICROSCOPES (AFMS) TO DIRECTLY PROBE THE RESPONSE OF A MATERIAL TO AN ELECTRICAL BIAS. HERE WE DEMONSTRATE THE UTILITY OF PFM FOR FAILURE ANALYSIS OF A MULTILAYERED CERAMIC CAPACITOR. THE PIEZORESPONSE OF THE DIELECTRIC WAS ANALYZED BY EVALUATING THE RESPONSE TO SWITCHING OF THE ELECTRIC FIELD. ADDITIONALLY, DISCONTINUOUS STRUCTURES IN THE DEVICE WERE IDENTIFIED, WHICH LIKELY HAD A DIRECT EFFECT ON DEVICE PERFORMANCE.

## INTRODUCTION

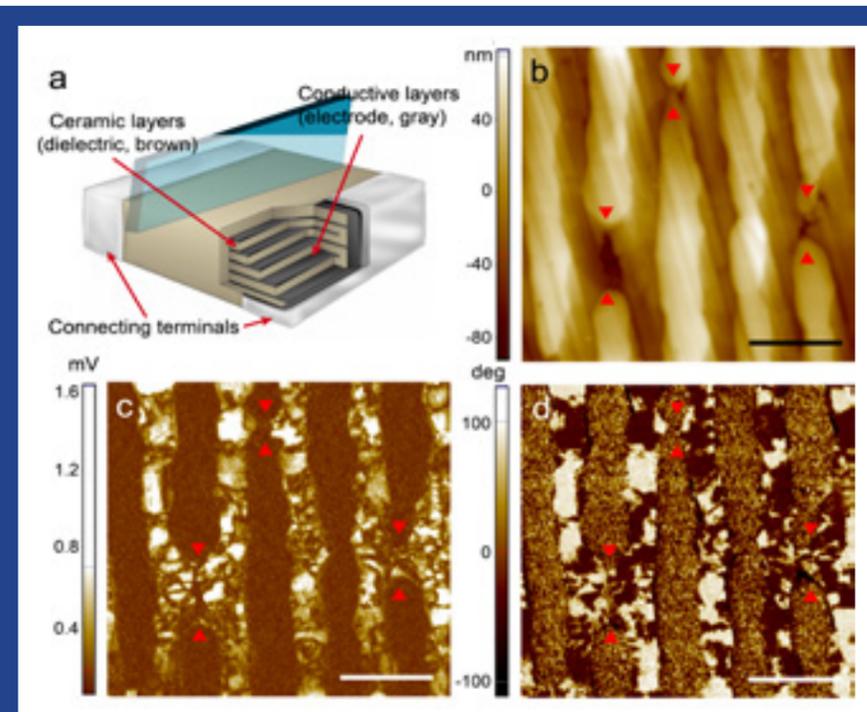
From renewable energy to electronics and biology, there are varieties of materials that exhibit a coupling of electrical and mechanical behavior. This coupling, known as a piezoelectric effect, is an intrinsic material property where the application of an electrical field induces a mechanical response. This material property is implemented in a multitude of applications ranging from ultrasonic imaging, to actuators and sensors.<sup>1</sup>

Common man-made piezoelectric materials

include ceramics such as barium titanate and lead zirconate titanate while polymers such as polyvinylidene fluoride also exhibit piezoelectric properties. Naturally occurring piezoelectric materials include bone, quartz, and DNA.

Piezoresponse force microscopy (PFM) is one of the most established non-destructive techniques to observe local electromechanical response at the nanometer length scale. PFM, also termed dynamic-contact electrostatic force microscopy (DC-EFM) by Park Systems,

is performed in an atomic force microscope (AFM) operating in contact mode with an electrically-biased conductive tip to probe local nanoscale displacements in response to electronic stimuli. These sample displacements are often very small with a low signal-to-noise ratio; therefore, a lock-in amplifier is connected to the deflection signal to selectively drive the desired frequency and by-pass unwanted signal. Since the AFM photodiode is position-sensitive, PFM can also identify the direction of electrical polarization in active piezoelectric or ferroelectric domains.



**Figure 2** The architecture and PFM results of the cross section of a MLCC. (a) A schematic of a MLCC device showing individual layers of the dielectric and electrode. The blue feature shows the plane that was cut to produce a cross section image show in panels b–d. (Image source: [http://www.tonarc.com/posts/kemet-news\\_3](http://www.tonarc.com/posts/kemet-news_3)) The (b) topography (c) PFM amplitude and (d) PFM phase images of the cross section of a MLCC. Scalebars: 2  $\mu\text{m}$ . Red arrowheads depict regions where the morphologies are discontinuous, suggesting device failure.

To capture this directionality, there are two distinct imaging modes: vertical PFM and lateral PFM (VPFM, LPFM) which are sensitive to domains polarized out-of-plane and in-plane, respectively.<sup>2</sup> (Fig. 1) Taking both vertical and lateral PFM components into account, one can identify the components of a local polarization vector to define the direction of the polarization vector using vector PFM.

**Vertical PFM** In VPFM, the cantilever will deflect normal to the sample surface in response to the applied bias, which indicates the presence of piezoelectric domains that point out-of-plane or normal to the sample surface (Fig. 1a-b). As a result, the EFM phase signal in the AFM will for example, appear bright for domains that point upward and dark for domains that point downward.

**Lateral PFM** In LPFM, to detect the piezoelectric domains that are pointed in-plane, the sample would exhibit a displacement shearing the surface. This lateral movement would result in a torsional displacement of the cantilever and would be detected by the position sensitive

photodiode as a lateral deflection indicating a polarization direction parallel to the sample surface (Fig. 1c-d).

**Vector PFM** In piezoelectric samples with arbitrary crystallographic orientations, the application of a tip bias will result in both in-plane and out-of-plane displacements. By simultaneously collecting both VPFM and LPFM signals, vector PFM can be performed to determine the final direction of the polarization vector in nanometer-sized grains. While piezoelectric constants of the material or a local orientation map can be obtained, most researchers assume that the local polarization orientation correlates with crystal orientation on the macro scale.<sup>3</sup>

It is also worthwhile to note that in a practical setting there are some limitations in combining vertical and lateral PFM signals, as crosstalk can arise from geometrical constraints of the cantilever. Additionally, tip displacement in the lateral direction can be underestimated compared to surface displacement of the sample due to effects such as friction.<sup>4</sup>

## MULTILAYER CERAMIC CAPACITORS

Since piezoelectric materials have both sensing and actuating properties, they have countless applications in the electronics industry.<sup>5</sup> In particular, ceramics such as barium titanate exhibit piezoelectric behavior and have proven to be robust dielectric materials in capacitors, as they are cost effective and exhibit high intrinsic dielectric constants along with resistance to humidity and temperature. Multilayer ceramic capacitors (MLCC) are produced in large quantities, with over a trillion (10<sup>12</sup>) barium titanate-based MLCCs manufactured each year.<sup>6</sup> They can be found in applications ranging from controlling the anti-lock brake system on a car to a heart monitor in a hospital. Society relies heavily on MLCCs to be dependable; however they can be susceptible to failure. For example, high temperatures from soldering or storage can cause thermal stress, resulting in cracking, increased current or shorts. A high-energy surge can also prove to be catastrophic and cause high leakage currents or rupture of the device itself. However, several of the devices may not pass specification after completing processing through the assembly line. To understand how the device fails whether during use, storage, or assembly, PFM is a powerful technique to analyze the functionality of devices, including MLCCs.

Here we report the analysis of a MLCC cross section using LPFM. We identify the discrete metal-dielectric domains within the device and we can also resolve regions within the dielectric material that exhibit unique polarization directions. Additionally, discontinuities in the individual materials can be observed in both topography and electrical signals, and likely affect device performance.

## EXPERIMENTAL

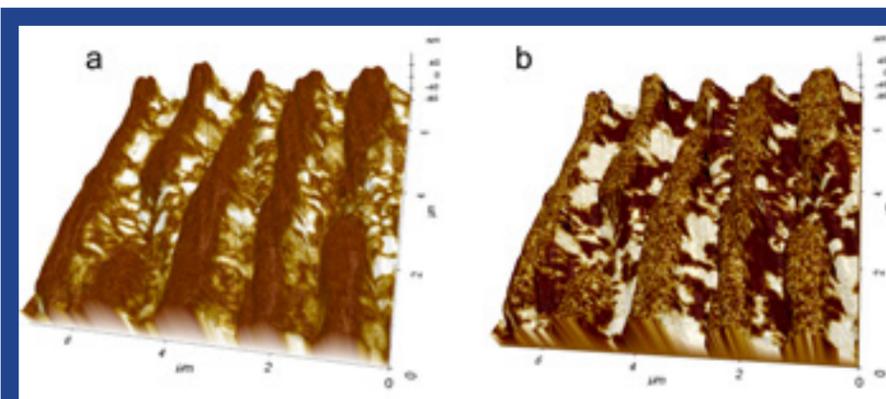
A cross section of a MLCC was analyzed using a Park NX20 AFM and the LPFM signal was acquired using a scan rate of 0.2 Hz. A conductive NANOSENSORSTM PointProbe® Plus-Electrostatic Force Microscopy (PPP-EFM) cantilever (nominal spring constant  $k = 2.8 \text{ N/m}$  and resonant frequency  $f = 25 \text{ kHz}$ ) coated with PtIr5 on both the front and back sides and nominal radius of curvature of 25 nm was used. The AFM tip was biased with 2V AC with no additional external bias applied to the sample during imaging.

## RESULTS AND DISCUSSION

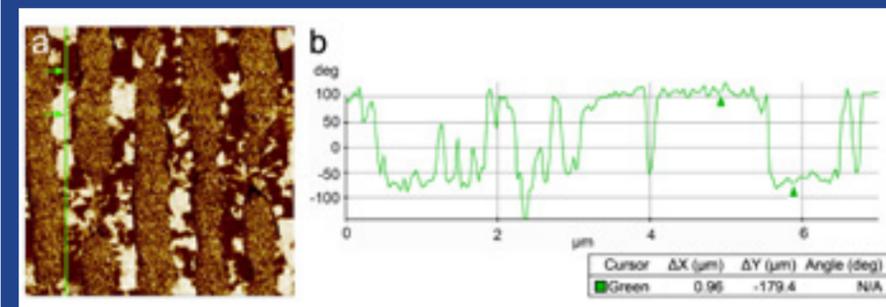
AMLCC is typically monolithic with an alternating dielectric (ceramic) and metal (electrode) layers that extend to corresponding connecting terminals at either end of the device (Fig. 2a). In this work, we characterize the cross section of a MLCC (cross section direction illustrated by the blue “slice” in Fig. 2a). The topography signal from this sample (Fig. 2b) shows alternating vertical structures that correlate to dielectric and electrode layers. These alternating structures also lose continuity from the top of the image to the bottom of the image and are noted in the images by red arrowheads. These discontinuities could be representative of a defect in the device. Additionally, faint diagonal striations can be observed that are likely due to sample preparation where mechanical polishing was performed.

To further investigate the piezoelectric response of the device, representative LPFM amplitude and phase images were acquired. The PFM amplitude signal (Fig. 2c) defines the local electromechanical activity of the sample surface and directly follows sample displacement that results due to the piezoelectric effect. External contributions such as capacitive cantilever-surface interactions or electrostatic contributions can result in artifacts to the electromechanical signal and efforts to minimize this effect provide better quality data. The PFM phase signal (Fig. 2d) provides information about the polarization vector of the individual domains. Specifically, the piezo-response will oscillate in-phase or out-of-phase when the polarization direction is parallel or antiparallel to the field, respectively.

The images acquired from the MLCC show regions that are taller in the topography image but lack amplitude or phase signals, suggesting that these regions do not exhibit piezoelectric behavior. Since the ceramic dielectric is known to be piezoelectric, this allows us to identify these non-responsive areas as regions containing the metal electrode. The dielectric layers also traverse the gaps in the electrode (Fig. 2, red arrowheads and Fig. 3), which would contribute to reduced device performance and could potentially result in a failure to meet specification. Additionally, the amplitude and phase images of the MLCC show multiple domains within the piezoelectric material. The appearances of bright or dark regions indicate a difference in the direction of



**Figure 3.** 3D representation of MLCC (a) PFM amplitude and (b) PFM phase overlaid with height images showing discontinuities in the electrode and dielectric material traversing the electrodes at these defect sites.

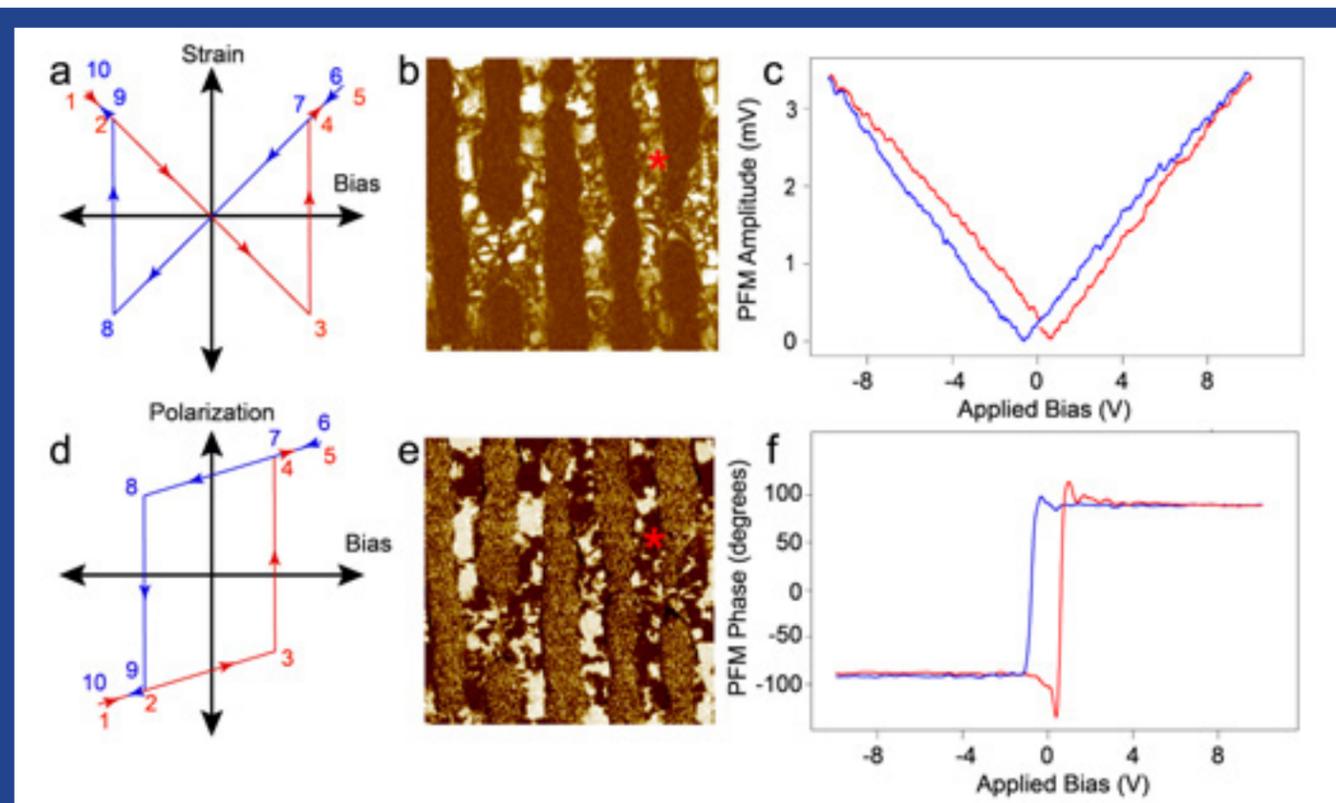


**Figure 4.** LPFM phase represents the polarization direction of in-plane ferroelectric domains. (a) The image with a vertical line and (b) the corresponding line trace. The green arrows show the difference between light and dark regions which show a 180° phase shift. This shift demonstrates that these domains have parallel and antiparallel polarization directions.

the polarization vector. The absolute direction of the vector (and meaning of bright and dark region in the phase image) will vary due to user setting such as the polarity of the applied bias. However, the domains that show a reversal in the phase signal (180°) as observed in Fig. 4 have opposite in-plane polarization directions (since LPFM is implemented here). Regions that show less than a 180° phase shift exhibit polarization directions that have both in-plane and out-of-plane components.

PFM is also capable of performing spectroscopy at defined locations to measure the response to switching electric fields and sample hysteresis (also known as switching-spectroscopy PFM). The local ferroelectric behavior of the domains in the MLCC is characterized in Fig. 5. Theoretical curves demonstrating the relationship between strain and electric field (Fig. 5a) and the relationship between polarization and electrical field (Fig. 5d) are shown for reference.<sup>7,8</sup> Since the amplitude directly measures the displacement of the sample, the strain response as a function of

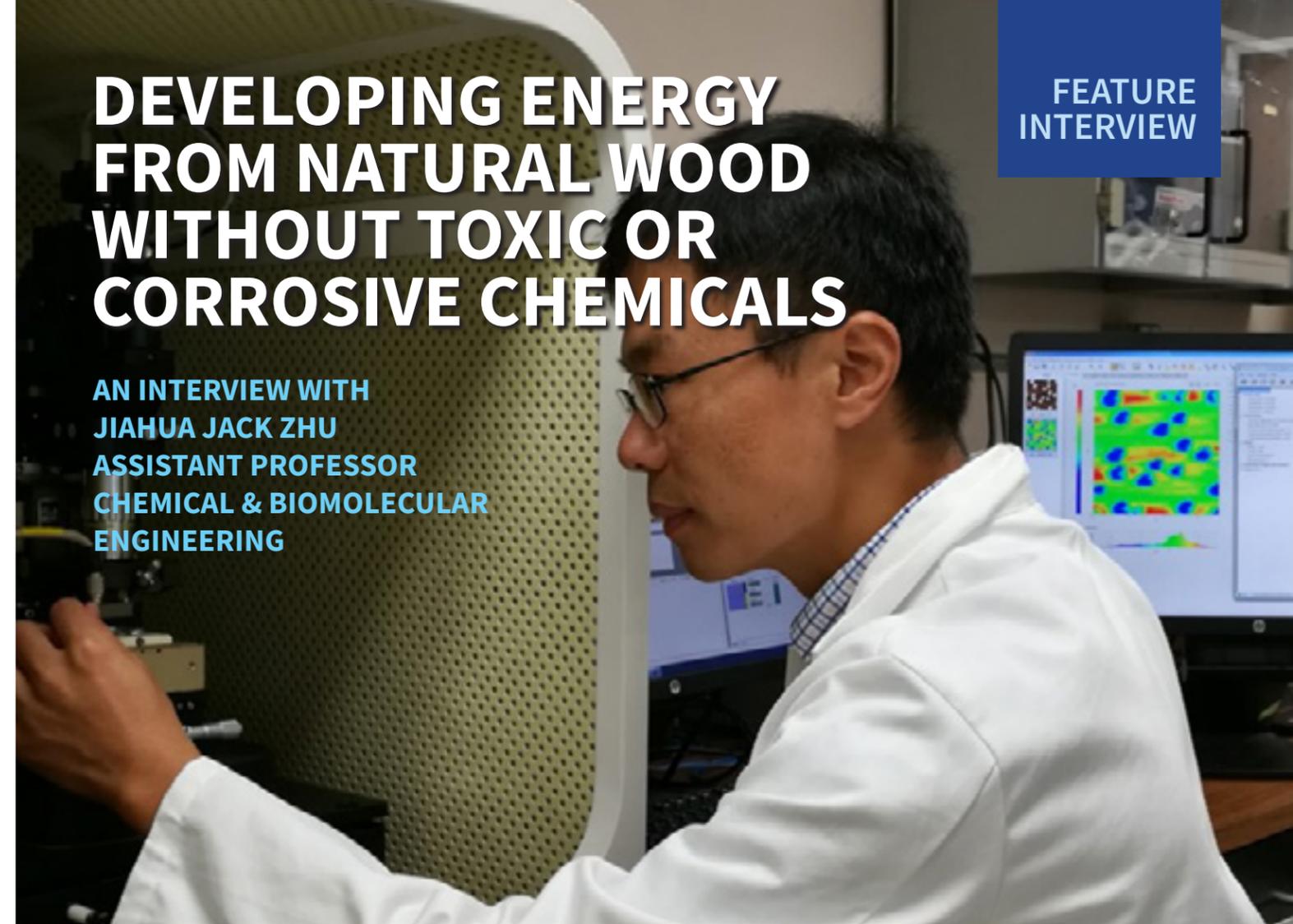
sample bias can be measured in the dielectric of the MLCC (Fig. 5b, asterisk). Fig. 5c shows a characteristic “butterfly” shape that is similar to the ideal strain versus bias curve. The coercive voltage, which is a measure of ability to withstand an external electric field without depolarizing, is 0.7 V (See figure caption for details). The theoretical hysteresis loop of the phase (or polarization) response of a ferroelectric material is shown in Fig. 5d. The true response of the MLCC dielectric with a sweeping electric field is shown in Fig. 5f demonstrates and sharp transition at the bias voltage of  $\sim 0.7 \text{ V}$ . The offset of this value between sweeping from a negative to positive voltage and back demonstrates retention performance of the material. Repeated polarization reversal could also provide information about ferroelectric fatigue. demonstrates and sharp transition at the bias voltage of  $\sim 0.7 \text{ V}$ . The offset of this value between sweeping from a negative to positive voltage and back demonstrates retention performance of the material. Repeated polarization reversal could also provide information about ferroelectric fatigue.



**Figure 5.** PFM switching spectroscopy on the dielectric material of a MLCC. (a) The theoretical strain-bias response from a ferroelectric material. 1-5 depicts the behavior with increasing bias and 6-10 shows the response to reducing bias. Points 3 and 8 on this curve provide the coercive voltage for the material. (b) The PFM amplitude image and the (c) corresponding “butterfly” shape of the amplitude as the electric field was swept from -9V to +9V (red) and back (blue). The red asterisk denotes the region that the spectroscopy was performed (d) The theoretical polarization-bias response from a ferroelectric material. 1-5 depicts the behavior with increasing bias and 6-10 shows the response to reducing bias. The distance between points 3 and 8 reflects retention performance of the material. (e) PFM phase image and (f) the corresponding phase behavior as the electric field was swept forward (red) and back (blue). The red asterisk denotes the location at which the spectroscopy was performed.

# DEVELOPING ENERGY FROM NATURAL WOOD WITHOUT TOXIC OR CORROSIVE CHEMICALS

AN INTERVIEW WITH  
**JIAHUA JACK ZHU**  
 ASSISTANT PROFESSOR  
 CHEMICAL & BIOMOLECULAR  
 ENGINEERING



HIGH SURFACE AREA MESOPOROUS CARBON IS SUCCESSFULLY MANUFACTURED FROM NATURAL WOOD VIA THIS GREEN TECHNIQUE UNDER DEVELOPMENT AT INTELLIGENT COMPOSITES LABORATORY, THE UNIVERSITY OF AKRON

## CONCLUSIONS

Here we demonstrated the use of LPFM to characterize the cross section of a MLCC. This technique enables nanoscale characterization of piezoelectric domains within the dielectric of the capacitor. The electrode was distinguished from the dielectric and discontinuities in the device were identified as regions that would be expected to compromise device performance. Both the response in strain (amplitude) and polarization (phase) as a function of applied bias were explored to evaluate material characteristics including hysteresis and coercive voltage. Overall, the ability to characterize the piezoresponse of materials at the nanoscale and quantify the

polarization vector of a material with applied electric field enables researchers to perform local electric measurements and establish structure-property relationships for multiple applications.

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## FEATURE INTERVIEW WITH JIAHUA JACK ZHU

### ASSISTANT PROFESSOR CHEMICAL & BIOMOLECULAR ENGINEERING

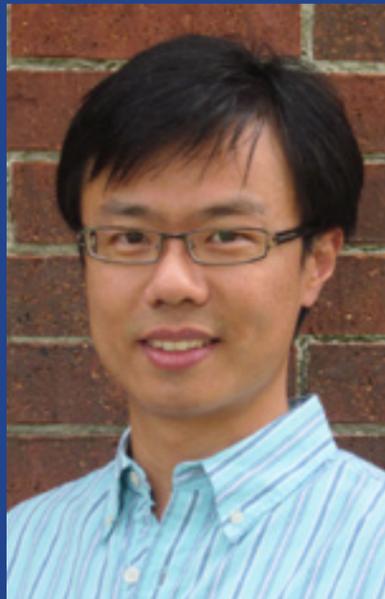
**Please explain briefly how carbon is manufactured from natural wood and why it is a "greener" method?**

The unique structured carbon is a replica of cellulose framework in the natural wood. Wood is like a building structure with steel frame (cellulose and hemicellulose) and concrete (lignin). By carbonizing the framework with a heat treatment process, the cellulose framework can be fixed as carbon framework.

Then, lignin is selectively removed to left porous framework structure behind. Different from conventional physical and chemical activation processes, where corrosive chemicals or high-temperature process up to 800 oC are required to generate micropores, our method does not involve any chemicals. All that is needed is nitrogen, air, and a carefully programmed heating profile. By the combination of these three elements, the porous structure of carbon can be easily tuned without involving chemicals.

**How does this process activate without corrosive chemicals?**

The use of corrosive chemicals in traditional processes is to etch out micropores and enlarge surface area. It is very challenging to generate inter-connected pore channels. We developed a mild oxidation process that interconnected pore channels can be created by hot air. The principle is similar but the process is more economic and environmental friendly.



## JIAHUA JACK ZHU, PhD

DEPARTMENT OF CHEMICAL & BIOMOLECULAR  
ENGINEERING, THE UNIVERSITY OF AKRON,  
AKRON, OHIO

Dr. Jiahua Zhu is an Assistant Professor in the Department of Chemical & Biomolecular Engineering at the University of Akron. Dr. Zhu received his Ph.D. degree in Chemical Engineering from Lamar University in 2013 and received a Master degree in Chemical Engineering from Nanjing University of Technology (2009) and Bachelor degree in Applied Chemistry from Yangzhou University (2006). Dr. Zhu's current research interest covers the fundamental study of multifunctional polymer- and carbon-based nanocomposites and explores their applications in emerging fields such as heat transport, energy storage, catalysis, environmental remediation, etc. Dr. Zhu has coauthored more than 100 peer-reviewed journal articles and three book chapters. His work has been cited more than 4,000 times with H index of 37. Dr. Zhu has actively served on TMS and AIChE societies as symposium organizer and session chair since 2011 and served as reviewer for more than 40 scientific journals. Dr. Zhu was awarded the Chinese Government Award for Outstanding Self-Financed Students Abroad, Young Leader Development Award from Functional Material Division of The Minerals, Metals & Materials Society, Early Career Award from Polymer Processing Society and Early Career Investigator Award from ECS Electrodeposition Division.

### Can this process be used on other biomass resources?

This is a general method can be used for a great variety of biomass resources. So far, we have demonstrated the effectiveness of this method in processing softwood, hardwood, cotton and bamboo into mesoporous carbon and more testing is on the way.

### How long will it be before this process is used in manufacturing?

We published our first research article in 2015 and immediately attracted industrial interests. A patent was filed (US 20160272502 A1) afterwards. Right now, we are working on the process optimization for better quality control of the porous carbon products. I would expect 2-3 years before it goes to manufacturing.

### How are magnetic nano composites used to remove metal from polluted water?

The greatest advantage of magnetic nanocomposites is its high adsorption efficiency and easy recycling. A well-known fact is that the smaller adsorbent usually comes with better adsorption capacity, while the separation and recycling of smaller adsorbent becomes more challenging. The magnetic nanoparticles embedded in bulk adsorbent can attract toxic heavy metal ions or reduce them to less toxic forms. Meanwhile, magnetic nanoparticles enable fast separation by external magnetic field.

### What are self organized Nano Crystals and why are they called the thermal highway?

Filler technology is widely adopted in the industry to produce thermally conductive materials. To reach satisfactory thermal conductivity, fillers need to be interconnected to cut off the thermal barrier between the particles. It can be done with extremely large fraction of fillers in matrix, however, the processability, materials cost and mechanical property of the composites will be sacrificed. Self-organized nanocrystals are thermal fillers that can be grown in polymer. The unique feature of this technology is to create interconnected crystal structure without interfaces. The phonon can be efficiently transported along the crystal structure without scattering. Therefore, such composite has great advantage in thermal conduction as compared to conventional composites.

### How does Atomic Force Microscope help you image your research?

Since composites hold a promising future in the thermal management area and the interface is the major thermal barrier in composites, the focus of our research is to understand the thermal transport behavior across different filler/matrix interfaces. By using Scanning Thermal Microscopy technique on Atomic force microscope platform, we can clearly identify cylindrical structure by Park's new 3D AFM is having a huge impact on the performance of vertical devices such as FinFET, TFET, STT-MRAM and others.

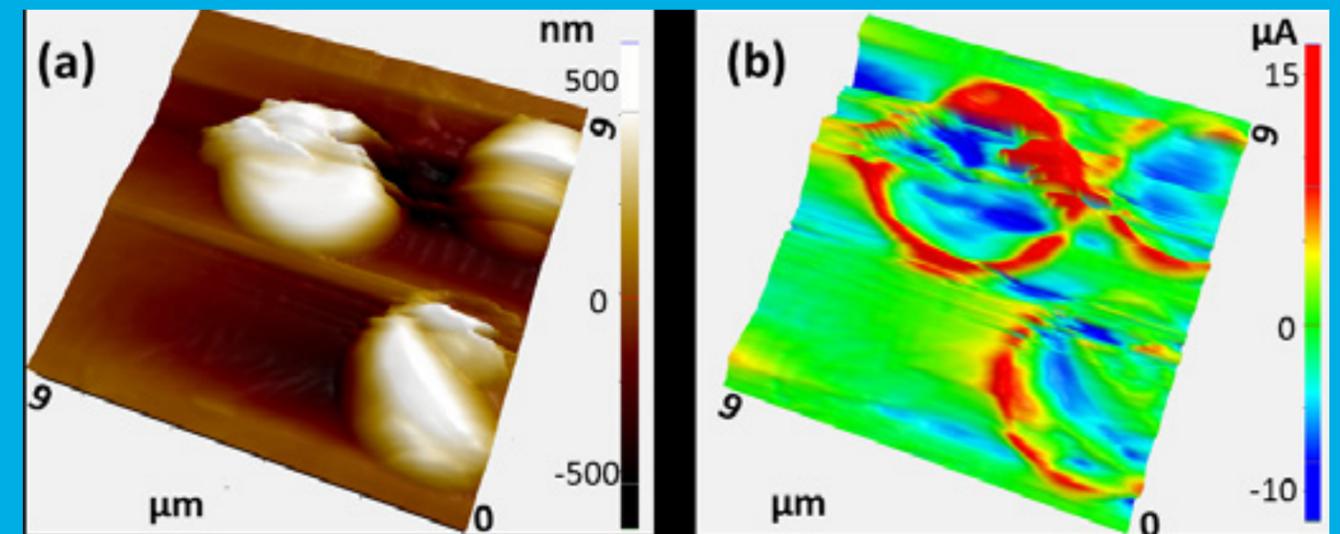


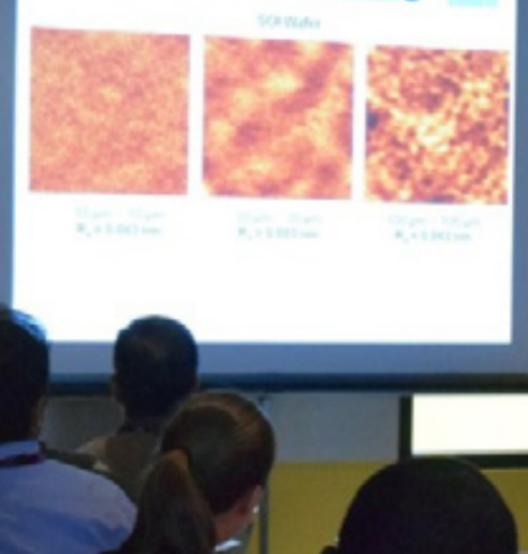
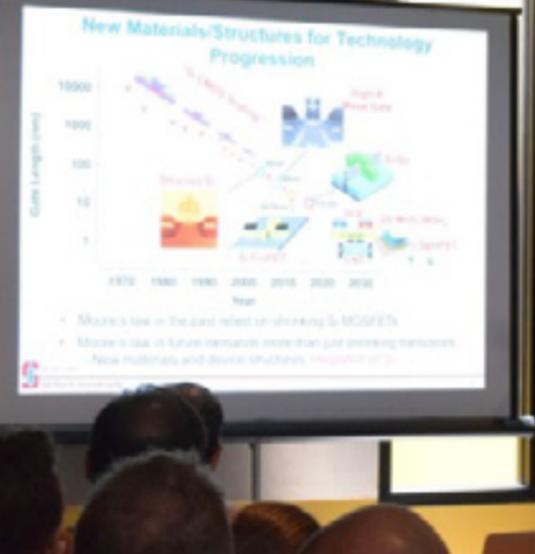
Figure 1. (a) AFM three-dimensional topography of PVA/amino acid crystal composites, (b) corresponding scanning thermal images.

**“BY USING SCANNING THERMAL MICROSCOPY TECHNIQUE ON AN ATOMIC FORCE MICROSCOPE PLATFORM, WE CAN CLEARLY IDENTIFY THE DISTRIBUTION OF THERMAL CONDUCTION AREAS SURROUNDING THE INTERFACE WHICH IS VERY IMPORTANT FOR GENERATING A FUNDAMENTAL UNDERSTANDING IN INTERFACIAL THERMAL TRANSPORT AND ENGINEERING MORE EFFECTIVE INTERFACES IN COMPOSITES.”**



# STANDING ROOM ONLY CROWD AT PARK SYSTEMS AFM SEMICON WEST LUNCHEON

PRESENTATIONS BY  
**DR. SANG-IL PARK, CEO OF PARK SYSTEMS AND  
 PROF. SARASWAT, STANFORD UNIVERSITY**



PROF. SARASWAT, THE RICKEY/NIELSEN PROFESSOR IN THE SCHOOL OF ENGINEERING AT STANFORD UNIVERSITY GAVE AN INFORMATIONAL TALK ENTITLED, "REAL LIMITS TO NANOELECTRONICS: INTERCONNECTS AND CONTACTS" TO A STANDING ROOM ONLY CROWD AT THE PARK SYSTEMS SEMICON WEST AFM LUNCHEON JULY 11, 2017 ABOUT FUTURE HIGH PERFORMANCE CHIPS, THE LATEST TECHNOLOGY FOR OPTICAL INTERCONNECTS AND OTHER INTERCONNECT INNOVATIONS.

HIS RESEARCH CURRENTLY INVESTIGATES NEW DEVICE STRUCTURES TO CONTINUE SCALING MOST TRANSISTORS, DRAMS AND FLASH MEMORIES TO THE NANOMETER REGIME, 3-DIMENSIONAL ICS WITH MULTIPLE LAYERS OF HETEROGENEOUS DEVICES, METAL AND OPTICAL INTERCONNECTS, AND HIGH EFFICIENCY AND LOW COST SOLAR CELLS.

ABOVE: DR. SANG-IL PARK, CEO AND FOUNDER OF PARK SYSTEMS SHARES HIS VISION FOR THE FUTURE OF AFM TECHNOLOGY FOR INDUSTRIAL NANOMETROLOGY AND THE LATEST TECHNOLOGICAL INNOVATIONS FROM PARK SYSTEMS AT THE PARK AFM LUNCHEON. "OUR PARTNERSHIP WITH MANY LEADING SEMICONDUCTOR INSTITUTIONS SUCH AS IMEC AND STANFORD PROVIDES A CRUCIAL LINK OF SCIENTIFIC COLLABORATION THROUGHOUT THE CHAIN OF SUPPLIERS AND VENDORS IN SEMICONDUCTOR WAFER PRODUCTION CREATING SIGNIFICANT TECHNOLOGICAL ADVANCES IN AFM-BASED INLINE NANOSCALE METROLOGY," STATED DR. SANG-IL PARK, CEO OF PARK SYSTEMS. "WE WERE EXCITED TO SHOWCASE THESE ADVANCES AT THIS YEAR'S SEMICON WEST SHOW AND GIVE HIGHLIGHTS AT OUR AFM LUNCHEON."

## REAL LIMITS TO NANOELECTRONICS: INTERCONNECTS AND CONTACTS

Modern electronics has advanced at a tremendous pace over the course of the last half century primarily due to enhanced performance of MOS transistors due to dimension scaling. Silicon bulk CMOS dominated the microelectronics industry in the past. However, future Si technology is reaching practical and fundamental limits. To go beyond these limits FinFETs have been introduced and novel device structures like surround gate FETs, TunnelFETs, etc. and potentially higher performance material like Ge, III-Vs, carbon nanotubes and 2D materials are being aggressively studied.

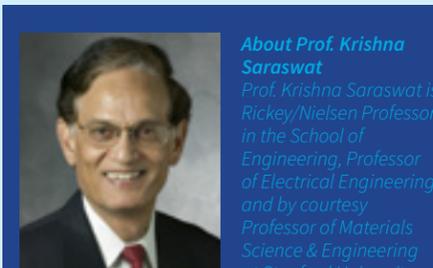
As device scaling continues, parasitic source resistance largely dominated by contact resistance is beginning to limit the device performance. Historically the method to reduce  $\rho_s$  is by increasing doping density thereby thinning the barrier, thus allowing more tunneling current. This method works well for n-Si and p-Ge which can be doped heavily. It is not very practical for n-Ge, p-Si, many III-Vs and 2D materials because of the inability to dope them heavily. There are many other alternatives to reduce contact resistance, such

as, metastable doping, Fermi level de-pinning and band engineered heterostructures.

While novel structures and materials have enhanced the transistor performance, the opposite is true for the interconnects that link these transistors. Looking into the future the relentless scaling paradigm is threatened by the limits of copper/low-k interconnects, including excessive power dissipation, insufficient communication bandwidth, and signal latency for both off-chip and on-chip applications. Many of these obstacles stem from the physical limitations of copper/low-k electrical wires, namely the increase in copper resistivity, as wire dimensions and grain size become comparable to the bulk mean free path of electrons in copper and the dielectric capacitance.

Thus, it is imperative to examine alternate interconnect schemes and explore possible advantages of novel potential candidates. This talk will address effects of scaling on the performance of Cu/low-k interconnects, alternate interconnect schemes: carbon

nanotubes (CNT), graphene, optical interconnect, three-dimensional (3-D) integration and heterogeneous integration of these technologies on the silicon platform.



**About Prof. Krishna Saraswat**  
 Prof. Krishna Saraswat is Rickey/Nielsen Professor in the School of Engineering, Professor of Electrical Engineering and by courtesy Professor of Materials Science & Engineering at Stanford University. He received Ph.D. from Stanford University and B.E. from BITS, Pilani, India. His research interests are in new and innovative materials, structures, and process technology of silicon, germanium and III-V devices and metal and optical interconnects for nanoelectronics, and high efficiency and low cost solar cells. Prof. Saraswat has supervised more than 85 doctoral students, 25 postdoctoral scholars and has authored or co-authored 15 patents and over 750 technical papers, of which 10 have received Best Paper Award. He is a Life Fellow of the IEEE. He received the Thomas Callinan Award from The Electrochemical Society in 2000, the 2004 IEEE Andrew Grove, Inventor Recognition Award from MARCO/FCRP in 2007, the Technovisionary Award from the India Semiconductor Association in 2007 and the Semiconductor Industry Association Researcher of the Year Award in 2012. He is listed by ISI as one of the 250 Highly Cited Authors in his field.

## NEW MATERIALS AND STRUCTURES FOR TECHNOLOGY PROGRESSION IN 3D HETEROGENEOUS INTEGRATION OF SEMICONDUCTOR DEVICES

### Q & A WITH PARK SYSTEMS RESEARCH SCIENTIST

**Can you explain more about what 3D crystallization refers to in regards to ICS fabrication technology? How far in the future do you think it will be before this becomes more commonly used?**

3D crystallization refers to a process where you take join a completed first level circuit and join it to a crystalline structure (e.g., another silicon wafer) that has been placed on top of it. This process is completed by using a technique like plasma-activated lower temperature wafer bonding. After completing a second level circuit on the newly placed crystalline structure through laser annealing, you could then add a third, fourth, etc. crystalline structure and continue building the IC vertically. This fabrication technology confers multiple benefits including reduced ICS power consumption, cost, and footprint, however, there are several challenges that need to be overcome before it becomes more commonly used. For starters, building up ICS systems vertically introduces cumulative heat buildup with each circuit level, the issue of trapped contamination between layers, and potential layer misalignment.

**What are 3D self-assembled devices? Do you know where research on these type of devices is being performed?**

3D self-assembled devices are created by influencing molecules to bind one another in large numbers to create 3D structures. This occurs all the time in biological processes and now we are applying research in related fields such as supramolecular chemistry to predict how and eventually get elements to self-assemble into structures useful for specific applications such as transistors on a semiconductor chip. Self-assembly is one of the holy grails of nanotechnology and is subsequently a very hot topic for research and industrial labs around the world to explore.

**How will advances in 3D integration affect our technology? Can you give some examples of future products or technologies that do not exist now but may once we achieve heterogeneous 3D integration on silicon platforms?**

3D integrated circuits are strongly considered to be answer to ever-growing market demands for continuously miniaturize and improve our electronics. As we select and optimize from the currently fragmented playing field of myriad 3D integration

techniques, we should see next-generation tech products with greater storage capacity, lower power requirements, more efficient thermal designs, higher brightness and more vivid displays and lighting, and faster networking throughput than ever before. For example, currently, smart watches are generally positioned in the market as fitness trackers or complementary devices to more powerful mobile devices like smart phones due to the watches' technical limitations. With advanced 3D integration capabilities, we may finally be able to untether next-generation smart watches and have them available as more stand-alone products than they currently are.

**How is Park AFM (or just AFM in general) used to advance the emerging and future technologies for 3D heterogeneous integration? Does AFM play an important role in helping advance these technologies more quickly and why?**

To perform the direct surface bonding of one wafer to another (as in 3D crystallization techniques), each of the wafers need to have exceptionally smooth surfaces with roughness values below 1 nm. Atomic force microscopy plays a significant role in obtaining surface roughness measurements of silicon wafers to be used in ICS fabrication.

## INTERVIEW WITH DR. SANG-IL PARK, CEO AND FOUNDER PARK SYSTEMS, WORLD-LEADING MANUFACTURER OF ATOMIC FORCE MICROSCOPES



**Question: Park Systems is the leading AFM technology for both academic and industrial users. What were the key factors for Park's enormous success in advancing AFM technology for both types of users who often have very different requirements?**



Answer: During the last 20 years, we have intensively developed the core technology of AFM, such as flat scan systems, True Non-Contact mode, and advanced software. We also had a master plan to develop a full line of products from basic research AFM to the high-end fully automated in-line AFM. Since all of our products were designed with the same concept, they share a common platform. For example, we develop and manufacture the flexure scanners that we use both in research AFM and industrial AFM. This enables our development and production teams to be cross-sectional and address both academic and industrial demands. This operation model allowed us to share the developments for each type of users with the other user classes. Hence, you can see a development on the academic model that was initially developed for an industrial user and vice versa.

**Question: Given your current position based on Moore's law and the future of the semiconductor industry, how can AFM contribute to the future advancements in semiconductor fabrication?**

Answer: Moore's law has become the model for the industry. The smaller dimensions and nodes have led to much more stringent requirements for metrology tools. For example, in order to maintain the signal to noise ratio in the measurements, there are more rigorous noise requirements for the in-line metrology tools. Our systems maintain

the best system noise levels in industry for AFM products from over a decade ago, therefore, when the node sizes shrink, our solutions were ready to address the new measurement requirements. While the scale-down in lateral dimension approaches to physical limit, the 3D devices with vertical integration open new opportunities. The applications for AFM are expanding from the traditional measurements to new sets of measurements. We see many new measurement requirements for AFM since the time we started our joint development program with imec.



*Park Systems and imec have had a Joint Development Program to develop new protocol to increase production yield and device performance for the semiconductor industry since Feb 2015. Pictured: Dr. Luc Van den hove (President & CEO, Imec) and Dr. Sang-il Park (Chairman & CEO, Park Systems) at the signing ceremony.*

**Question: You mentioned the joint development program between Park Systems and imec. Can you share an example of the exciting contributions from this partnership?**

Answer: One excellent example was presented at ASMC 2017 where it was very well received. The AFM is used as an in-line monitoring solution for local height variations of SADP Fin heights and oxide recess in copper pads. This measurement provides crucial information required in the wafer-to-wafer hybrid bonding process. AFM was chosen over other metrology techniques due to its non-destructive measurement and sub-nanometer accuracy. The within wafer uniformity and wafer to wafer comparison can be performed using automated in-line AFM. The measurements with AFM are final and do not require any

post-measurement modeling. Hence, the short time-to-solution makes it a valuable method for decision making in process control.

**Question: AFM systems are perceived to be too slow for semiconductor device manufacturing for in-line metrology. However, Park AFM systems are being utilized for uniformity studies along with the wafers and dies manufacturing. How challenging is it to perform such measurements?**

Answer: Traditional AFMs are slow in acquiring images. However, the latest AFMs from Park Systems with high frequency cantilevers can scan much faster. Combined with bi-lateral scan and optimized navigation, our in-line AFM can meet the throughput requirement. Since AFM can measure actual dimensions directly, AFM has been a reference measurement system for fab. Now, with the level of automation, our users see more and more benefit in utilizing AFM for uniformity studies. Not only the throughput is significantly improved, time-to-solution and data reliability are exceptional comparing to other metrology solutions.

**Question: Park Systems has been growing solidly since their IPO in 2015. What is the relationship between the observed growth and the current AFM technology innovations at Park Systems?**

Answer: The AFM technology innovation we achieved in the past resulted in our revenue growth and made the IPO possible. Since the public offerings, we accelerated all of our activities including the R&D. I am confident that the current AFM technology innovation at Park Systems will generate greater revenue growth in the future. We have a passion for addressing new metrology challenges and making our customers happy.



## USING SKPM WITH PARK AFM TO ANALYZE ELECTRICAL PROPERTIES OF METAL, SEMICONDUCTOR DEVICE SURFACES, ORGANIC AND BIOLOGICAL MATERIALS

# HOW TO OBTAIN SAMPLE POTENTIAL DATA FOR SKPM MEASUREMENT

HOSUNG SEO, DAN GOO, AND GORDON JUNG, PARK SYSTEMS

## INTRODUCTION

Scanning Kelvin probe microscopy, or SKPM, was introduced as a tool to measure the local contact potential difference between a conducting atomic force microscopy (AFM) tip and the sample, thereby mapping the work function or surface potential of the sample with high spatial resolution. Since its first introduction by Nonnenmacher [1], SKPM has been used extensively as a unique method to characterize the nanoscale electrical properties of metal or semiconductor surfaces and semiconductor devices. Recently, SKPM has also been used to study the electrical properties of organic materials, devices [2–4], and biological materials. To eliminate any confusion, let us look into SKPM's synonyms for this technique:

- **SKPM: Scanning Kelvin Probe Microscopy**
- **KPFM: Kelvin Probe Force Microscopy**
- **SSPM: Scanning Surface Potential Microscopy**
- **SKFM: Scanning Kelvin Force Microscopy**
- **SP-AFM: Surface Potential Atomic Force Microscope**

## MICROSCOPY

SKPM will be used in this document, as it is the most widely used descriptor for this technique. The term 'Kelvin force' refers to similarities between this microscopic technique and the macroscopic technique, which is the Kelvin probe method. However, the methodology is somewhat different, but the measured value is equivalent for both techniques. For clarity, this note will refer only to the microscopic technique SKPM.

## FUNDAMENTALS OF SKPM

The SKPM measures Contact Potential Difference (CPD) between a conducting AFM tip and a sample. The CPD (VCPD) between the tip and sample is defined as:

(2.1) where  $\phi_{\text{sample}}$  and  $\phi_{\text{tip}}$  are the work functions of the sample and tip, and  $e$  is the electronic charge. The different Fermi energy levels between the AFM tip and sample surface causes an electrical force as the AFM tip is brought close to the sample surface. Figure 1 shows the energy level diagram of the tip and sample surface when sample and tip are different. Figure 1(a) depicts the energy levels of the tip and sample surface when separated tip and sample surface are close enough for electron tunneling, equilibrium of the states require Fermi levels to line-up at steady state. Upon electrical contact, the Fermi levels will align through electron current flow, and the system will reach to an equilibrium state as shown in Figure 1(b). The tip and sample surface will be charged, and an apparent VCPD will be formed (note, the Fermi energy levels are aligned but the

vacuum energy levels are no longer the same, and a VCPD between the tip and sample has been formed). An electrical force acts on the contact area, due to the VCPD. As shown in Figure 1(c), this force can be nullified. This technique is the Kelvin Probe method that relies on the detection of an electric field between a sample material and probe material. The electric field can be varied by the voltage VCPD, that is applied to the sample relative to the probe. If an applied external bias (VDC) has the same magnitude as the VCPD with opposite direction, the applied voltage eliminates the surface charge in the contact area.

The applied VCPD nullifies the electrical force and has the same value as the work function difference between the tip and the sample. This allows the work function of the sample to be calculated when the work function of the tip is known.

By applying an AC voltage (VAC) plus a DC voltage (VDC) to the AFM tip, SKPM measures the work function of the sample. VAC generates the oscillating electrical forces between the AFM tip and sample surface, and VDC nullifies the oscillating electrical forces that originated from CPD between the tip and the sample surface. The electrostatic force ( $F_{\text{es}}$ ) between the AFM tip and sample is given by:

(2.2) where  $z$  is the direction normal to the sample surface,  $\Delta V$  is the potential difference between VCPD and the voltage applied to the AFM tip, and  $dC/dz$  is the gradient of the capacitance between tip and sample surface. The external potential,  $V_{\text{Ext}}$ , is an additional voltage that is applied either to

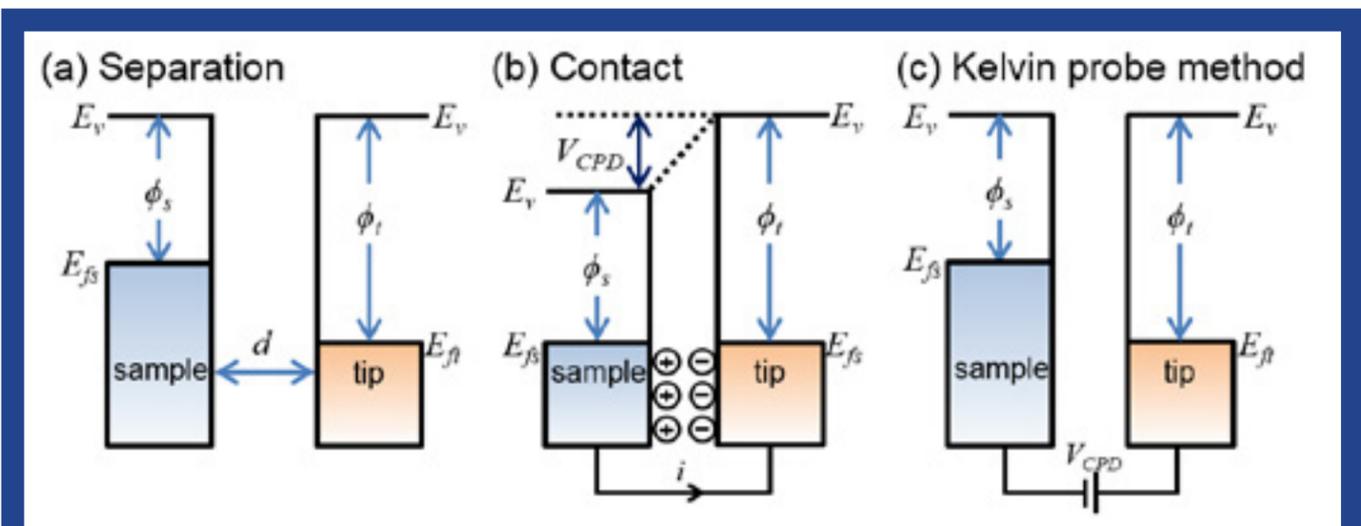


Figure 1. Electronic energy levels of the sample and AFM tip for three cases: (a) tip and sample are separated by distance  $d$  with no electrical contact, (b) tip and sample are in electrical contact, and (c) external bias (VDC) is applied between tip and sample to nullify the CPD and, therefore, the tip-sample electrical force.  $E_v$  is the vacuum energy level.  $E_{fs}$  and  $E_{ft}$  are Fermi energy levels of the sample and tip, respectively.

the tip or to the sample; the sign in front of  $V_{Ext}$  is explained below. The voltage difference  $\Delta V$  will be [5]:

**(2.3)** The amplitude of the tip vibration,  $V_{ac}$ , is proportional to the force  $F$ . Substituting the expression of the voltage given in Equations 2.2 and 2.3 and collecting the terms according to their frequencies, the following form for the amplitude of the tip vibration is obtained:

**(2.4)** This equation can be divided into three parts:

**(2.5)(2.6)(2.7)** FDC (Equation 2.5) results in a static deflection of the AFM tip.  $F_{\omega}$  with frequency  $\omega$  (Equation 2.6) is used to measure the VCPD, and  $F_{2\omega}$  is used for capacitance microscopy [6].  $F_{\omega}$  is electrical force component modified with frequency  $\omega$ .

It is also the function of VCPD and VAC. When electrostatic forces are applied to the tip by VAC with  $V_{Ext}$ , additional oscillating components (due to the electrical force) will be superimposed to the mechanical oscillation of the AFM tip. A lock-in amplifier is employed to measure the VCPD, to extract the  $F_{\omega}$ . The output signal of the lock-in amplifier is directly proportional to the difference between VCPD and  $V_{Ext}$ . The VCPD value can be measured by applying  $V_{Ext}$  to the AFM tip, such that the output signal of the lock-in amplifier is nullified and  $F_{\omega}$  reaches zero. Subsequently, the value of  $V_{Ext}$  is obtained for each point on the sample surface and maps the work function or surface potential of the whole sample surface area. The contact potential difference, VCPD, is obtained by the following procedure: the direct current VDC voltage,  $V_{Ext}$ , is varied until the

alternating current VAC vibration of the tip at the frequency  $\omega$  is nullified; at this voltage  $V_{Ext} = \pm V_{CPD}$ .

When the external voltage is applied to the tip or to the sample it changes their work functions. Hence, based on Equation 2.1 the sign of VCPD will be different in the two cases. The posteriori dc voltage difference (direction) VCPD is thus given for the two cases as:

**(2.8)(2.9)** where Equations 2.8 and 2.9 are for the cases of voltage applied to the sample and the tip, respectively. After the nullifying procedure, i.e., when VCPD, we obtain  $V_{Ext} = \pm V_{CPD}$ , where the '+' and '-' refer to the external bias applied to the sample and the tip, respectively.

### SKPM MODE FOR PARK SYSTEMS

There are various methods of measuring the SKPM mode in AFM. Among them, Park Systems uses two frequencies as shown in Figure 2. Two implemented lock-in amplifiers in the controller are used for each frequency moderation. One frequency is used to oscillate the cantilever and obtain a surface image using bimorph, which is the term for oscillating the cantilever using piezoelectric material. The other frequency directly signals the cantilever at 17.0 kHz, which is the frequency generally used for SKPM.

The topography signal and potential signal are acquired from each frequency simultaneously and two images are created without affecting each other. This allows the user to obtain a surface image and a potential image with a single scan. The topography signal is obtained by keeping the distance constant between the tip and the sample. The potential signal is obtained by applying a default external voltage and the experimentally determined work function values of the cantilever as described in Figure 2.

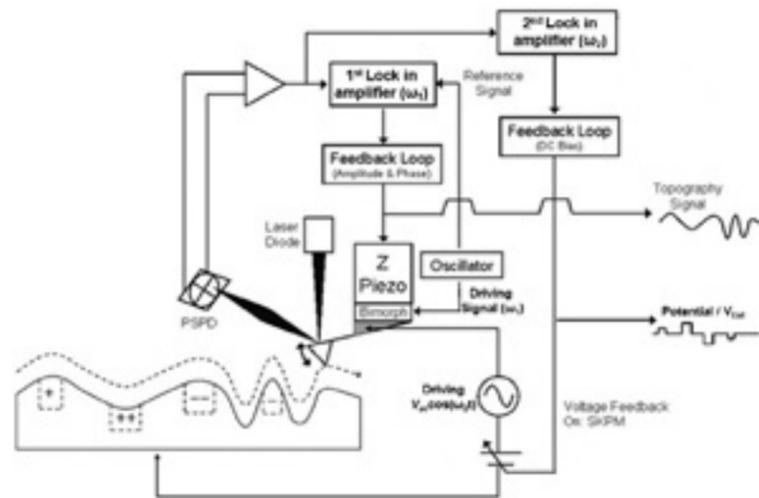


Figure 2. SKPM schematic used by Park Systems. Figure 3 (e) is the line profile data of the mean values for 16 adjacent points along the  $y$ -axis. It can be seen in the metal regions in the potential difference ( $V_{Ext}$ ) image that they are mutually inverted. This proves that the inverted signs, positive and negative expressions in Equations 2.8 and 2.9 are correct.

NCHA cantilever of NANOSENSORS was used for SKPM measurement. This model has a metallic layer coated on both sides of the cantilever and has a typical tip radius of curvature smaller than 50nm. The resonant frequency and force constant is 330 kHz and 42N/m, respectively. Here, the offset between the tip and the surface sample may occur as shown in Figure 3(e). The cause for this offset is the electrical factors that occur from the VAC amplitude. Therefore, to know the offset in the SKPM measurement, it is necessary to measure the HOPG or a calibration sample, which has work function values that are known in advance. One point is to be noted—the difference between the Au and Al areas must be constant according to the applied direction because there is an absolute difference in work function.

### ANALYSIS & REPEATABILITY ABOUT SKPM

The purpose of SKPM is to obtain the work function for the measuring specimen, not the VCPD between the tip and the sample. Therefore, accurate analysis is essential. To obtain the exact work function of the sample, it is necessary to measure several cantilevers and average them to obtain more accurate work function values of the samples. Calibration of the system must be done by using a sample that has a work function that is already known, for instance HOPG. First, a precise tip's work function must be measured using the sample with a given work function. This process is done to eliminate the electrical offset that could possibly happen during SKPM measurement. Secondly, after measuring the SKPM of the sample, the work function of the tip is obtained by using Equation 2.10. Finally, repeating this process several times and averaging the results will produce more accurate results.

The sample consisted of three different materials: Au, Si, and Al. For the calibration surface sample, Au was selected to become the base material. The work function of Si and Al were determined as explained above. The theoretical work function values and the experimentally determined work function values of Si and Al are shown in Table 1.

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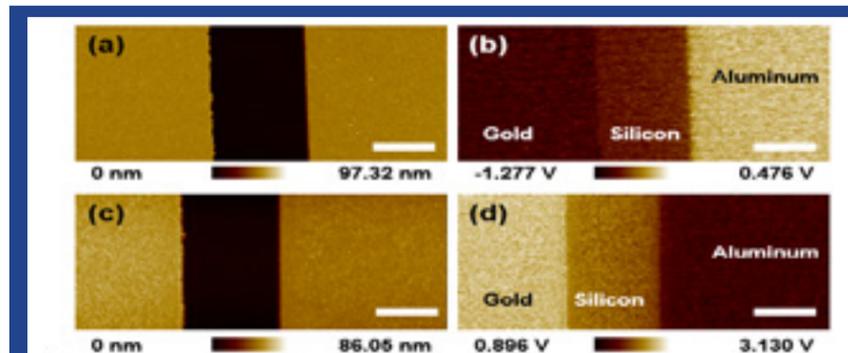


Figure 3. 25.0  $\mu$ m x 12.5  $\mu$ m SKPM images of the Au-Si-Al patterned sample. When applied to cantilever direction topography (a) and  $V_{Ext}$  (b). When applied to sample direction topography (c) and  $V_{Ext}$  (d). Scale bar is 5  $\mu$ m. (e) is a  $V_{Ext}$  (potential difference) line profile according to the applied function.

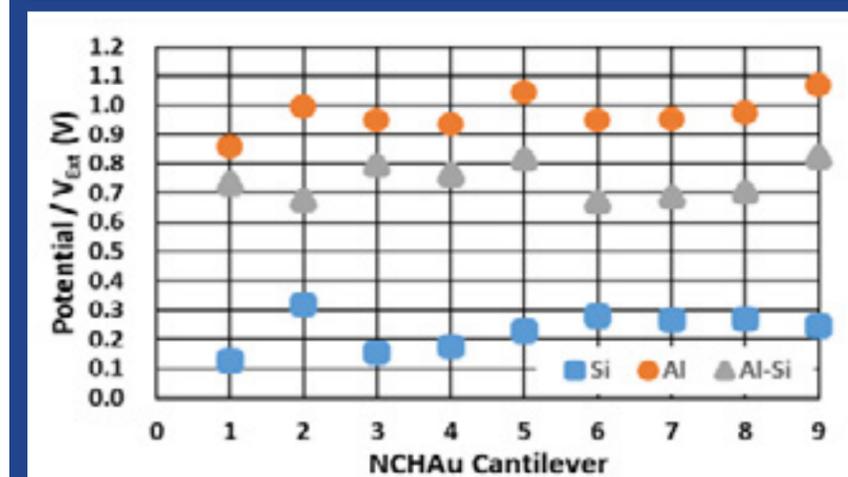
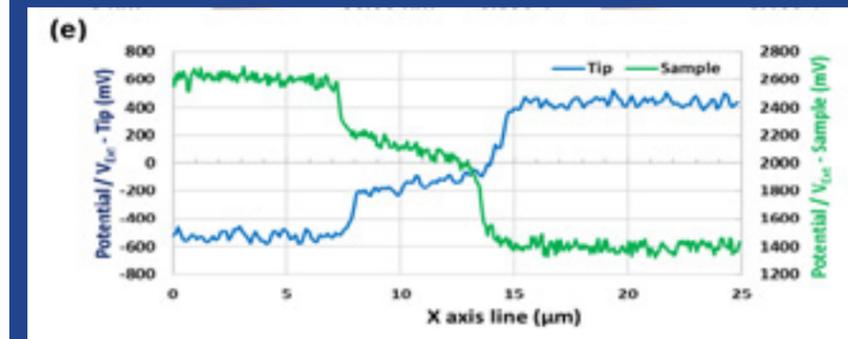


Figure 4. SKPM data obtained using nine different NCHAu (NANOSENSORS) probes on the Au-Si-Al patterned sample. The value on Al (orange circles), Si (blue squares) and their differences (gray triangles) are plotted

Material	Theoretical value (eV)	SKPM measured value (eV) 9 probes average
Gold (Au)	5.10 ~ 5.47	5.1 (Fix)
Silicon (Si)	4.60 ~ 4.85	4.87
Aluminum (Al)	4.06 ~ 4.26	4.13

Table 1. Theoretical work function values and nine different NCHAu probes work function values for average for each of the three materials in the Au-Si-Al patterned sample. Park Systems offers a suite of SKPM measurement solutions that serve as a quantitative work function measurement

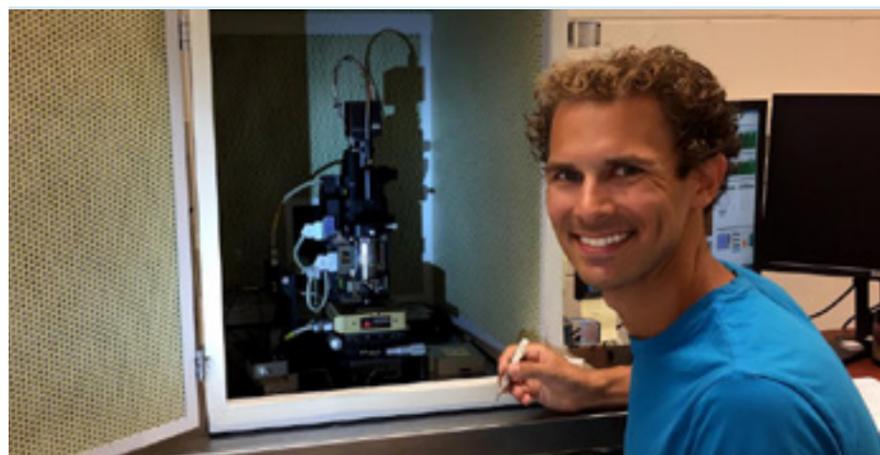
# PARK SYSTEMS OFFERS ATOMIC FORCE MICROSCOPE (AFM) SCHOLARSHIP

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two monetary scholarships to promote the education of future scientists and engineers in a number of nanoscale research areas that require advanced nano microscopy for analysis and to promote shared research findings and methodologies amongst researchers.

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## RECENT PARK AFM SCHOLARSHIP AWARD WINNERS



### JAMEY GIGLIOTTI

PHD CANDIDATE GEORGIA INSTITUTE OF TECHNOLOGY, SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

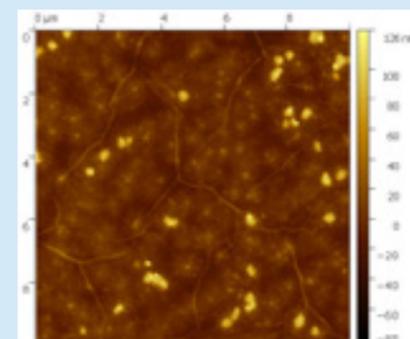
Jamey Gigliotti is a PhD candidate at the Georgia Institute of Technology in the School of Materials Science and Engineering. He began his tenure at Georgia Tech studying the growth of nanoscale piezoelectric films before joining the Epitaxial Graphene Lab where he continues to work in close collaboration with researchers at Georgia Tech Lorraine in Metz, France. Before coming to Georgia Tech, Jamey completed his undergraduate education at Penn State University, a few hours from his hometown of Harrisburg, Pa. While at Penn State, he worked on piezoelectric micromachined ultrasonic transducers for medical imaging and sonotweezing applications. This research took him to Germany to work with ultrasound

simulation experts. While the focus of his research has changed several times, a unifying theme has been the deposition and characterization of nanoscale material systems. He plans to continue along this theme, but with a new focus after graduation.

**1. Summarize the research you are doing and explain briefly how it will impact society. Why is your research important?**

Nanoelectronics are a pervasive technology, but have not undergone a transformative technology change in decades. Epitaxial graphene, a single layer of carbon atoms arranged in a honeycomb lattice on a single crystal SiC substrate, is a promising technology

platform to disrupt the silicon industry due to its unique electronic transport and robust thermal and chemical stability. However, despite billions of dollars in research, graphene technology has not trickled into industrial products, largely due to the need to reliably integrate graphene with dielectric and semiconducting materials to make useful and reliable electronics. Boron nitride, a dielectric isomorph to graphene, is an ideal candidate material which has been shown to preserve the electronic transport of graphene. Yet, to date, a scalable method to produce graphene-BN heterostructures has not been found. My research focuses on developing novel deposition techniques to enable epitaxial growth of boron nitride layers directly on pristine graphene surfaces, a necessary step to achieving industrially relevant graphene-based nanoelectronics.



A 20 nm thick boron nitride film deposited on a monolayer of epitaxial graphene. This topographical AFM image shows the pleated BN surface which is indicative of a 2D layered structures due to the negative in-plane coefficient of thermal expansion.



### XIN YIN

PHD CANDIDATE IN THE DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING AT UNIVERSITY OF WISCONSIN-MADISON

**“PARK AFM PROVIDES US WITH A HIGH-RESOLUTION AND RELIABLE MEASUREMENT OF THE THICKNESS AT THE SUB-NANOMETER LEVEL.”**

**2. What is the most useful part of using Park AFM for your research? Please explain what features are most useful and why?**

Graphene and BN are both 2D materials and demand a unique suite of characterization tools including scanning probe, electron microscopy, diffraction, and optical techniques. Scanning probe techniques are highly sensitive to surface topography and chemical states. As such, the Park AFM provides us with a direct probe of the individual atomic layers and can aid in differentiating SiC, buffer layer, graphene, and boron nitride regions, which is extremely difficult with scanning electron microscopy. For this, lateral force microscopy (LFM) is vitally important and can identify nanoscale regions of graphene and boron nitride from the SiC substrate. Graphene and boron nitride, both sp<sup>2</sup> bonded materials, interact only very weakly with the tip compared to SiC, which provides a stark imaging contrast. This information aids in our understanding of how these domains nucleate and grow, which guides the development of our custom deposition tools and processing conditions to achieve higher quality materials with more control over their morphology.



Xin Yin is currently a PhD candidate in the department of Materials Science and Engineering at University of Wisconsin-Madison. He joined Professor Xudong Wang's group in 2012. His research interests include study of growth kinetics in various ZnO nanostructures, and synthesis and electronic properties of nanometer-thick 2D ZnO nanosheets.

**1. Summarize the research you are doing and explain briefly how it will impact society. Why is your research important?**

Two-dimensional (2D) nanomaterials, with just one or a few atomic layers, exhibit physical properties dissimilar to those of their bulk counterparts. However, the current 2D materials have been largely limited to naturally layered materials, like graphene and transition metal dichalcogenides.

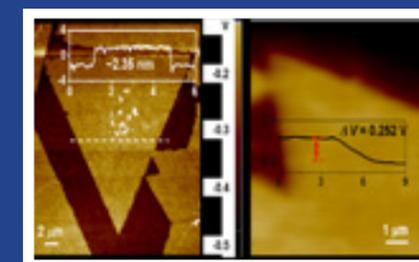
My research mainly focuses on the growth of two dimensional non-layered materials. With a unique growth method, single-crystalline nanometer-thick ZnO nanosheets with the size up to 20 micrometers are realized at water-air interface with surfactant monolayer as a template. More importantly, the thickness of ZnO nanosheets could be tuned from one unit cell to four unit cells.

This is the first time to realize the growth of ultrathin ZnO nanosheets. On one hand, it provides an opportunity to study the electronic, photonic, and mechanical properties emerging from the ultrathin feature of ZnO. For example, our investigation has found that the work function shows monoclinic increase with nanosheet thickness. This thickness-dependent work function provides a good flexibility in designing heterojunctions

with tunable band alignment. On the other hand, the research presents a strategy to boost the abundance of 2D materials through applying the unique growth method to other material systems.

**2. What is the most useful part of using Park AFM for your research? Please explain what features are most useful and why?**

Since we focus on the synthesis of 2D nanomaterials, the characterization on the thickness of the nanosheets is important. Park AFM provides us with a high-resolution and reliable measurement of the thickness at the sub-nanometer level. Moreover, to locate at one specific position for the measurement of electrical properties, as well as the mapping measurement, such as the surface potential mapping and current mapping, provides a chance to recognize and investigate the property difference from point to point.



Park NX20 300mm - first research AFM on the market capable of scanning the entire sample area of 300 mm wafers using a 300 mm vacuum chuck while keeping the system noise level below 0.5Å which opened up a whole new scope of measurement automation on a 300 mm wafers

Above, Left, topography image of one ZnO nanosheets, showing the thickness of ~2.35 nm. Right, contact potential difference (CPD) measurement of one ZnO nanosheets on Au-coated Si substrate, showing the CPD is ~0.252 V.[1]

## Park NX12

The most versatile  
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- *Built on proven Park AFM performance*
- *Equipped with inverted optical microscope*

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