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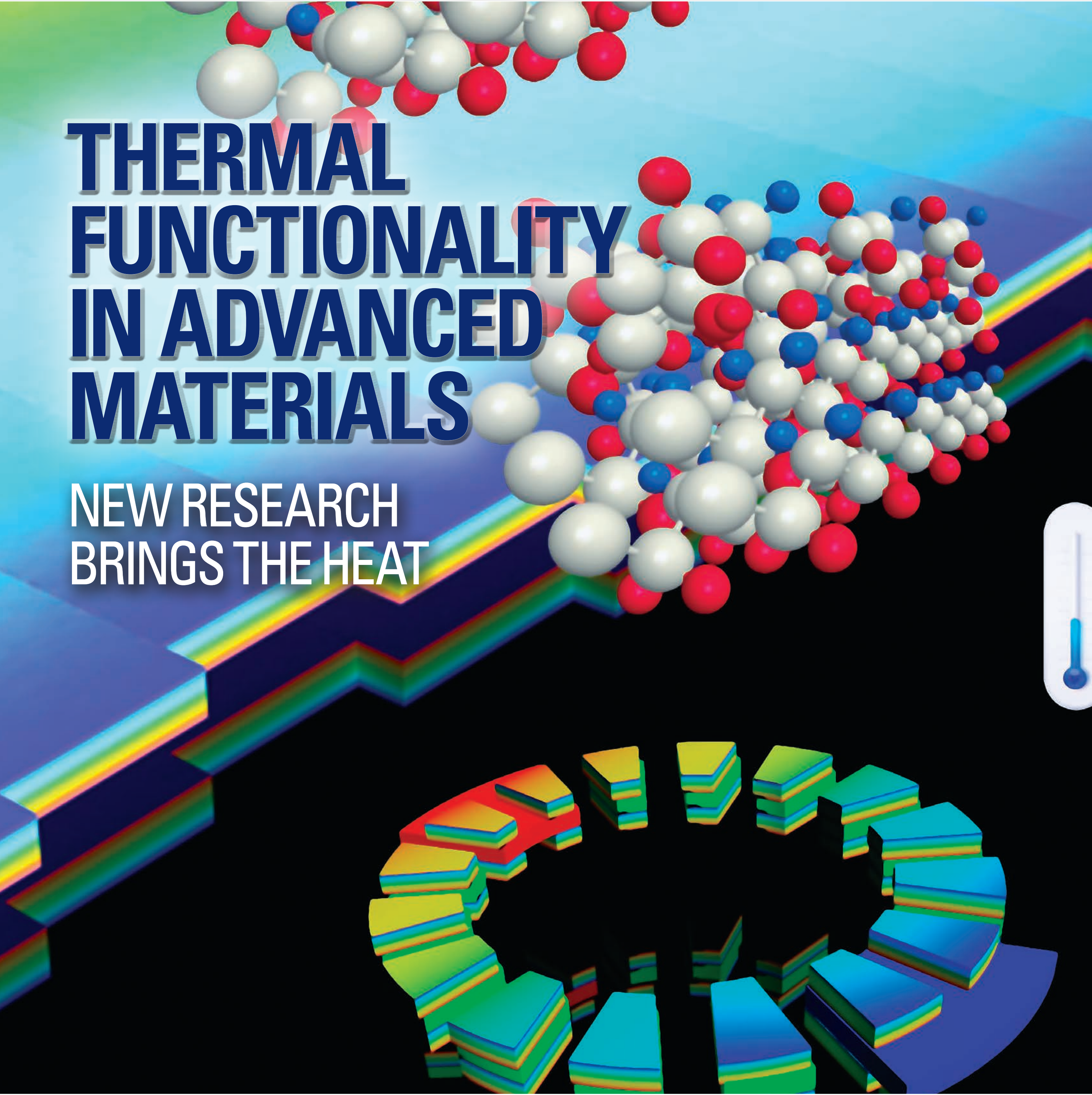
FOCUS on MATERIALS

MATERIALS RESEARCH INSTITUTE BULLETIN FALL 2015



THERMAL FUNCTIONALITY IN ADVANCED MATERIALS

NEW RESEARCH BRINGS THE HEAT

PennState
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Message from the Director

Clive Randall

Over the past several months, MRI has been engaged in strategic planning in conjunction with the University's planning. Our plan will guide us as we implement our goals in the 2016-2020 timeframe. I would like to take this opportunity to lay out the three fundamental principles that we have identified as crucial to our strategy in this period.

First and foremost, MRI is dedicated to the principle of scientific excellence. This includes not just highly cited papers in top rank journals, but emphasizes excellence in the education of the next generation of scientists and engineers who pass through our labs.

Next, we are dedicated to making an impact on industry. That means we will be a partner with companies that come to us for our expertise. This may involve the particular knowledge of individual faculty, in which case we will facilitate that partnership in whatever way we can. But it also means making industry partners welcome in our open labs and solving problems that only MRI has the unique facilities and expertise to address. We already have partnered with more than 400 companies a year in our Materials Characterization and Nanofabrication user facilities, but we can have an even greater impact with our industry friendly IP policies that make working with Penn State and MRI the simplest process of any university in the nation. We are also forging new relationships with our Behrend campus in the industrial hub of Erie, PA. Penn State Behrend has proven that they know how industry works, and together, we will enhance the competitiveness of a sizable segment of U.S. manufacturing, in particular, in areas of metal processing and polymer injection molding.

Third, we will become a central hub for humanitarian materials engineering in the U.S. This means we will use MRI's expertise in materials science and engineering to make a difference in the lives of people across the globe. This ambitious goal is driven by the desire of students, faculty, and our staff to contribute solutions to problems such as food security, clean water availability, and affordable healthcare in resource poor regions of the world. We have dedicated a section of each issue of this magazine to telling the stories that come out of this initiative.

Finally, this issue of *Focus on Materials* introduces an emerging field of research within MRI and Penn State, one that we believe in the years ahead will provide us scientific leadership in the growing science of functional thermal materials and devices. In functional materials, there has been major emphasis on electrical conduction, cross-coupled properties such as electromechanical behavior, mechanical properties, and electron and/or magneto optical properties, and far less emphasis on thermal transport and heat capacity. With greater awareness of thermal management in electrical devices, housing, transportation, etc., we need to expand our intelligence and investigations into the nature of heat functionality in new materials and integrated material design. If major breakthroughs can be made, developing markets in and around pure electricity will benefit from these innovations.

Sincerely,

Clive Randall

Director of the Materials Research Institute
and Professor of Materials Science and Engineering

To access the materials expertise at Penn State, please visit our Materials Research Institute website at **www.mri.psu.edu** or the Office of Technology Management website at **http://www.research.psu.edu/offices/otm**

Focus on Materials is a bulletin of the Materials Research Institute at Penn State University. Visit our web site at **www.mri.psu.edu**

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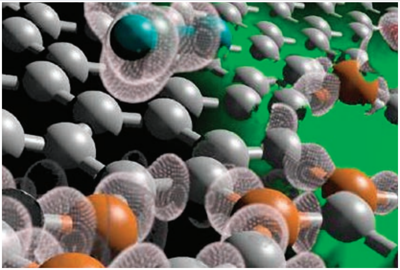
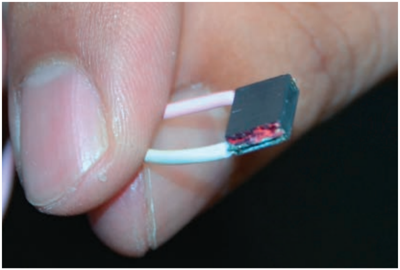
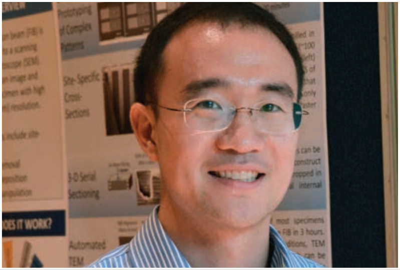






IN THIS ISSUE:

THERMAL FUNCTIONALITY IN ADVANCED MATERIALS

Cover: A schematic of an electrocaloric device being developed at Penn State Credit: Zhang Lab/Penn State

Snapshots are brief summaries of significant materials-related breakthroughs by MRI researchers. More information is available by visiting the links at the end of each summary.

A FAST CELL SORTER SHRINKS TO CELL PHONE SIZE

Commercial fluorescence activated cell sorters have been highly successful in the past 40 years at rapidly and accurately aiding medical diagnosis and biological studies, but they are bulky and too expensive ($200,000 -$1,000,000) for many labs or doctors' offices. Most significantly, these types of cell sorters can present biohazard concerns for operators and may damage cells or alter their properties, making them unfit for further study. To address these issues, researchers at Penn State have developed a new lab-on-a-chip cell sorting device based on acoustic waves.

In the cover story in the current issue of the British journal *Lab on a Chip*, researchers in the Department of Engineering Science and Mechanics at Penn State, along with Ascent Bio-Nano Technologies and the National Heart, Lung, and Blood Institute, a part of the National Institutes of Health, describe an acoustic cell sorter capable of the kind of high sorting throughput necessary to compete with commercial fluorescence activated cell sorters.

“The current benchtop cell sorters are too expensive, too unsafe, and too high-maintenance. More importantly, they have very low biocompatibility. The cell-sorting process can reduce cell viability and functions by 30–99 percent for many fragile or sensitive cells such as neurons, stem cells, liver cells and sperm cells,” said Tony Jun Huang, Penn State professor of engineering science and mechanics and the paper's corresponding author. “We are developing an acoustic cell sorter that has the potential to address all these problems.”

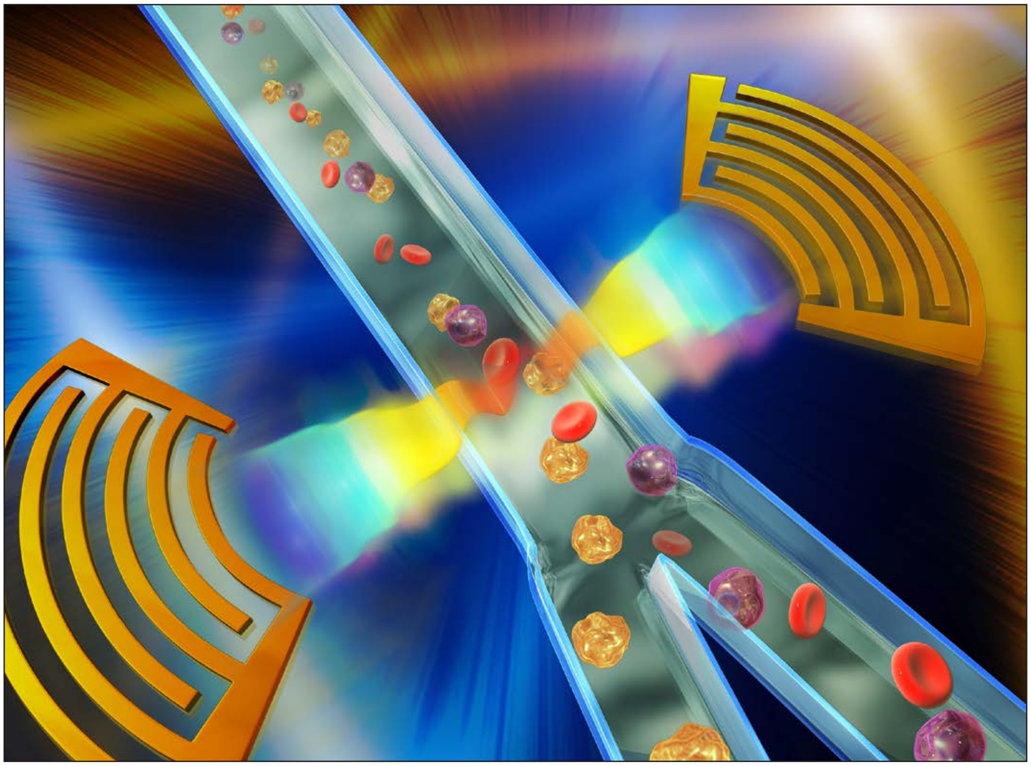


Illustration of blood components being separated by sound waves
Image: Tony Jun Huang/Penn State

The Penn State system can sort about 3,000 cells per second, with the potential to sort more than 13,000 cells per second. The speed is generated by using focused interdigital transducers to create standing surface acoustic waves (SSAWs). When the waves are not focused, the acoustic field spreads out, slowing the sorting process. The narrow field allows the sorting to take place at high speed while gently manipulating individual cells.

Because the device is built on a lab-on-a chip system, it is both compact and inexpensive – about the size and cost of a cell phone in its current configuration. With the addition of optics, the device would still be only as large as a book. The acoustic cell sorter was fabricated in Penn State's Nanofabrication Laboratory using standard lithography techniques.

"To the best of our knowledge, our device demonstrates the fastest operation time among all existing acoustic cell sorters," said Liqiang Ren, a graduate student in Huang's group and the paper's lead author.

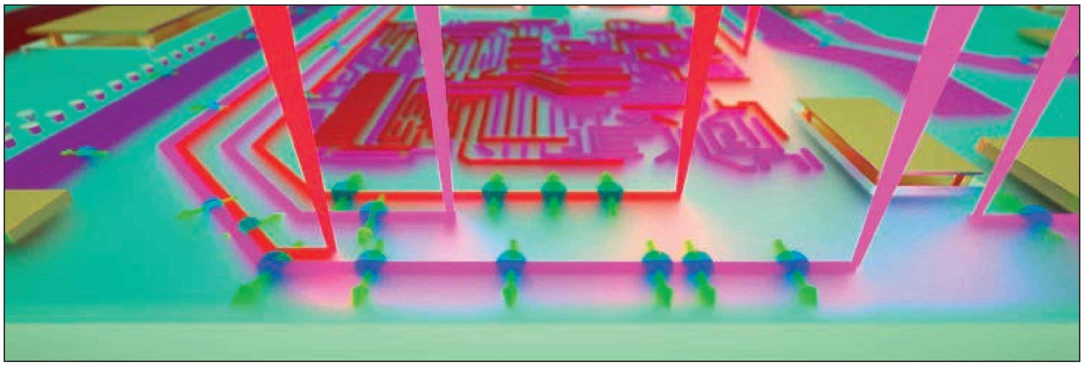
In future work, the researchers plan to integrate their acoustic cell-sorting unit with an optical cell-detecting unit with the goal of increasing throughput to 10,000 events per second.

Additional authors on the paper titled "A high-throughput acoustic cell sorter" are Yuchao Chen, Peng Li, Zhangming Mao, Po-Hsun Huang, Joseph Rufo and Feng Guo, all of Penn State, Lin Wang of Ascent Bio-Nano Technologies and Philip McCoy and Stewart J. Levine, National Heart, Lung, and Blood Institute. Funding was provided by the National Institutes of Health, the National Science Foundation, and the Penn State Center for Nanoscale Science. Portions of the work were performed at the Penn State Nanofabrication Laboratory, a node of the NSF-funded National Nanotechnology Infrastructure Network.

Contact Tony Jun Huang at junhuang@psu.edu or (814) 863-4209.
For the full story, visit mri.psu.edu/news/

CHANCE EFFECT OF LAB'S FLUORESCENT LIGHTS LEADS TO DISCOVERY

An accidental discovery of a "quantum Etch-a-Sketch" that may lead to the next generation of advanced computers and quantum microchips has been made by a team of scientists from Penn State University and the University of Chicago.



Artist's rendition of optically-defined quantum circuits in a topological insulator Image: Peter Allen

The researchers accidentally discovered a new way of using beams of light to draw and erase quantum-mechanical circuits on topological insulators, a unique class of materials with intriguing electronic properties.

The research, led by Nitin Samarth, professor and Downsbrough Head of Physics at Penn State, and David D. Awschalom, Liew Family Professor and deputy director in the Institute of Molecular Engineering at the University of Chicago, was published in the October 9 issue of Science Advances, an online journal of the American Association for the Advancement of Science.

The electrons in topological insulators have unique quantum properties that many scientists believe will be useful for developing spin-based electronics and quantum computers. However, making even the simplest experimental circuits with these materials has proved difficult because traditional semiconductor engineering techniques tend to destroy their fragile quantum properties. Even a brief exposure to air can reduce their quality.

The researchers discovered an optical effect that allows them to "tune" the energy of electrons in these materials using light, without ever having to touch the material itself. They have used this effect to draw and erase one of the central components of a transistor – the p-n junction – in a topological insulator for the first time.

Like many advances in science, the path to this discovery had an unexpected twist. "To be honest, we were trying to study something completely different," said Andrew Yeats, a graduate student in Awschalom's laboratory and the paper's lead author. "There was a slow drift in our measurements that we traced to a particular type of fluorescent lights in our lab. At first we were glad to be rid of it, and then it struck us – our room lights were doing something that people work very hard to do in these materials."

The researchers found that the surface of strontium titanate, the substrate material on which they had grown their samples, becomes electrically polarized when exposed to ultraviolet light, which their room lights happened to emit at just the right wavelength. The electric field from the polarized strontium titanate was leaking into the topological insulator layer, changing its electronic properties

The research was supported by the U.S. Office of Naval Research, Air Force Office of Scientific Research, and Army Research Office.

Contact Nitin Samarth at nxs16@psu.edu. For the full story by Barbara Kennedy in the Eberly College of Science visit mri.psu.edu/news/.

ULTRASENSITIVE SENSORS MADE FROM BORON-DOPED GRAPHENE

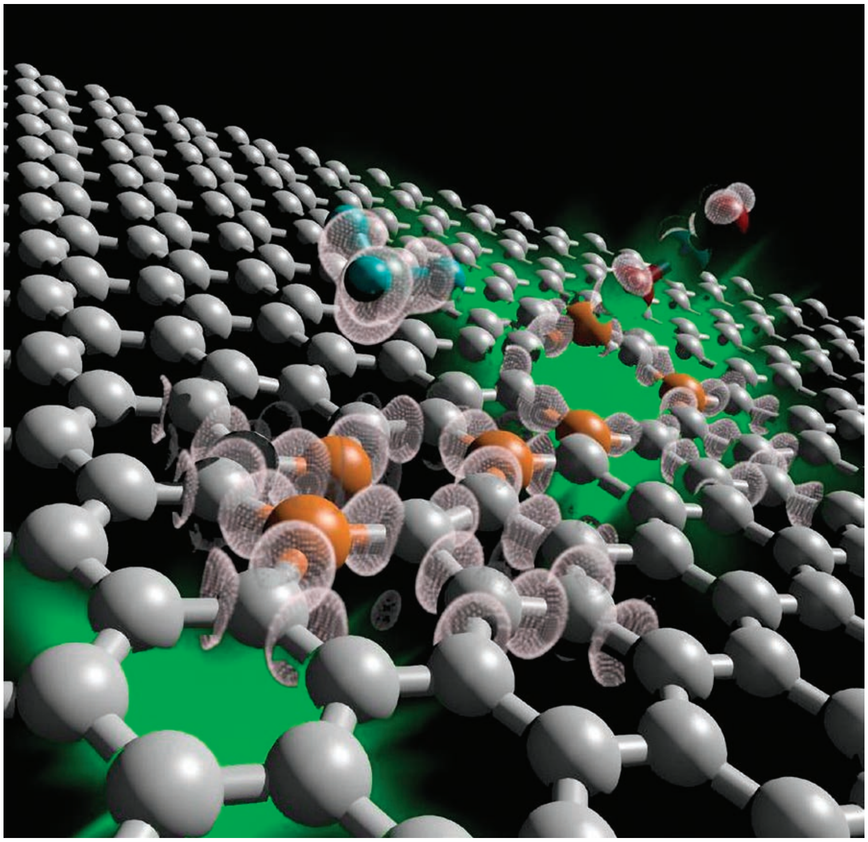
An international team of researchers, led by Penn State, has developed ultrasensitive gas sensors based on the infusion of boron atoms into the tightly bound matrix of carbon atoms known as graphene. The group is composed of researchers from six countries and includes the 2010 Noble laureate and graphene pioneer Konstantin Novoselov, and Morinobu Endo, the discoverer of carbon nanotubes.

Graphene is well known for its remarkable strength and ability to transport electrons at high speed, but it is also a highly sensitive gas sensor. By adding boron atoms, the boron graphene (BG) sensors were able to detect noxious gas molecules at extremely low concentrations, parts per billion in the case of nitrogen oxides and parts per million for ammonia, the two gases tested to date. This translates to a 27 times greater sensitivity to NOx and a 105 times greater sensitivity to ammonia compared to pristine graphene. The researchers believe these results, reported in the current issue of the *Proceedings of the National Academy of Sciences*, will open a path to high-performance sensors that can detect trace amounts of many other molecules.

“This is a project that we have been pursuing for the past four years. We were previously able to dope graphene with atoms of nitrogen, but boron proved to be much more difficult,” said Mauricio Terrones, professor of physics, chemistry and materials science at Penn State and the paper’s corresponding author. “Once we were able to synthesize what we believed to be boron graphene, we collaborated with experts in the United States and around the world to confirm our research and test the properties of our material.”

Both boron and nitrogen lie next to carbon on the periodic table, making their substitution feasible. But boron compounds are very air sensitive and decompose rapidly when exposed to the atmosphere. One-centimeter-square sheets were synthesized at Penn State in a one-of-a-kind bubbler-assisted chemical vapor deposition system. The result was large-area, high quality B-doped graphene sheets.

These sensors can be used for labs and industries that use ammonia, a highly corrosive health hazard, or to detect NOx, a dangerous atmospheric pollutant emitted from automobile tailpipes. In addition to detecting toxic or flammable gases, theoretical work indicates that boron-doped graphene could lead to improved lithium ion batteries and field effect transistors, the authors report.



Boron atoms (orange) in a lattice of graphene (gray) sense gas molecules on the graphene surface. Credit: Terrones Lab/Penn State

The lead authors of the PNAS paper, "Ultrasensitive gas detection of large-area boron-doped graphene," are Ruitao Lv, a former post-doctoral scholar in Terrones lab now at Tsinghua University, Beijing, China; Gugang Chen, a senior scientist of Honda Research Institute USA Inc.; Andrés Botello-Méndez, Catholic University of Louvain la-Neuve; and Amber McCreary, a graduate student in Terrones' lab.

Support for this work was provided by the National Natural Science Foundation of China, MURI awards from the U.S. Air Force Office of Scientific Research, Honda Research Institute USA Inc., Europe's Graphene Flagship, and Penn State's Center for Nanoscale Science, a National Science Foundation MRSEC, and Penn State's Materials Research Institute.

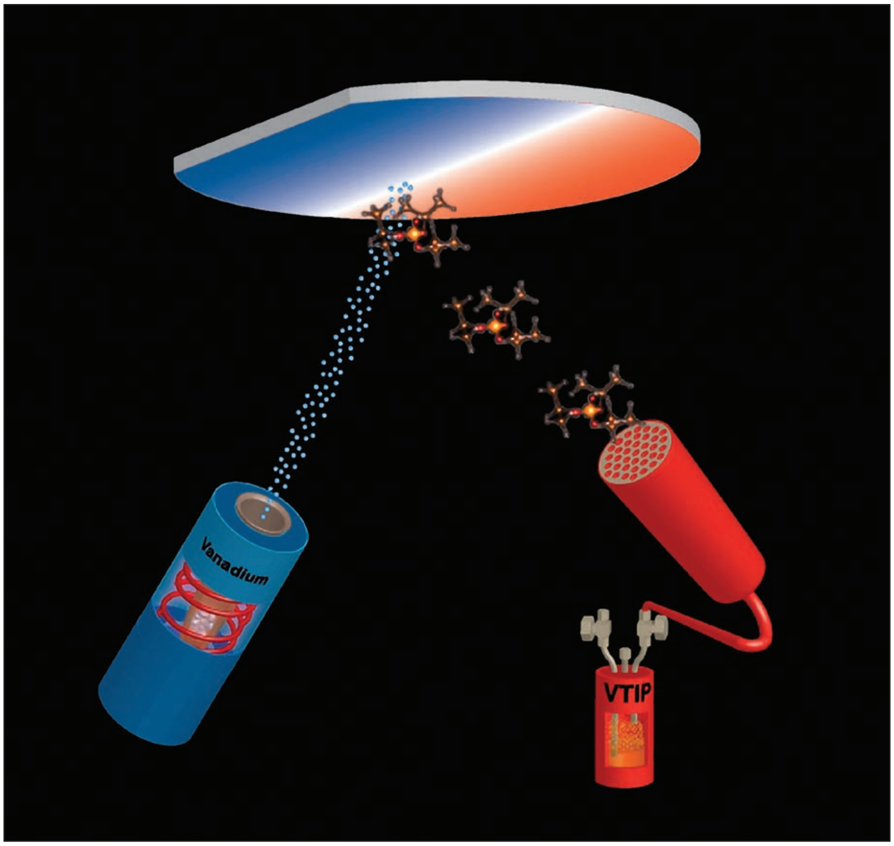
Contact Mauricio Terrones at mut11@psu.edu. For the full story, visit mri.psu.edu/news/.

ELECTRONICS GET A POWER BOOST WITH THE ADDITION OF SIMPLE MATERIAL

The tiny transistor is the heart of the electronics revolution, and Penn State materials scientists have just discovered a way to give the workhorse transistor a big boost, using a new technique to incorporate vanadium oxide, one of a family of materials called functional oxides, into the device.

"It's tough to replace the current transistor technology, because semiconductors do such a fantastic job," said Roman Engel-Herbert, assistant professor of materials science and engineering. "But there are some materials, like vanadium oxide, that you can add to existing devices to make them perform even better."

The researchers knew that vanadium dioxide, which is just a specific combination of the elements vanadium and oxygen, had an unusual property called the metal-to-insulator transition. In the metal



Vanadium atoms (blue) and molecules containing vanadium oxide (orange) coat a 3 inch sapphire wafer. Credit: Penn State MRI state, electrons move freely, while in the insulator state, electrons cannot flow. This on/off transition, inherent to vanadium dioxide, is also the basis of computer logic and memory.

The researchers had the idea that if they could add vanadium oxide close to the transistor it could boost the transistor's performance. Likewise, by adding it to the memory cell, it could improve the stability and energy efficiency to read, write and maintain the information state. The major challenge they faced was that vanadium dioxide of sufficiently high quality had never been grown in a thin film form on the scale required to be of use to industry, the so-called wafer scale. Although vanadium dioxide, the targeted compound, looks simple, it is very difficult to synthesize. In order to create a sharp metal-to-insulator transition, the ratio of vanadium to oxygen needs to be precisely controlled. When the ratio is exactly right, the material will show a more than four-order-of-magnitude change in resistance, enough for a sufficiently strong on/off response.

In a paper in the online journal Nature Communications, the Penn State team reports for the first time the growth of thin films of vanadium dioxide on 3-inch sapphire wafers with a perfect 1:2 ratio of vanadium to oxygen across the entire wafer. The material can be used to make hybrid field effect transistors, called hyper-FETs, which could lead to more energy efficient transistors. The implementation of vanadium dioxide can also benefit existing memory technologies, a quest that Penn State researchers are actively pursuing.

The current paper's lead author, Hai-Tian Zhang, a PhD student in Engel-Herbert's group, said, "To determine the right ratio of vanadium to oxygen, we applied an unconventional approach in which we simultaneously deposit vanadium oxide with varying vanadium-to-oxygen ratios across the sapphire wafer. Using this 'library' of vanadium-to-oxygen ratios, we can perform flux calculations to determine the optimal combination that would give an ideal 1:2 vanadium/oxygen ratio in the film. This new method will allow a rapid identification of the optimal growth condition for industrial applications, avoiding a long and tedious series of trial-and-error experiments."

"Wafer scale growth of VO_2 thin films using a combinatorial approach," was coauthored by graduate students Hai-Tian Zhang, Lei Zhang, Debangshu Mukherjee, Ryan Haislmaier, and assistant professors Nasim Alem and Roman Engel-Herbert, all in the Department of Materials Science and Engineering and the Materials Research Institute at Penn State, and Yuan-Xia Zheng a graduate student in Penn State's Department of Physics. (http://dx.doi.org/10.1038/ncomms9475)

The work was supported by the National Science Foundation and the Penn State Center for Nanoscale Science. Analysis and measurement was performed in the Penn State Materials Characterization Laboratory, a facility of the Materials Research Institute.

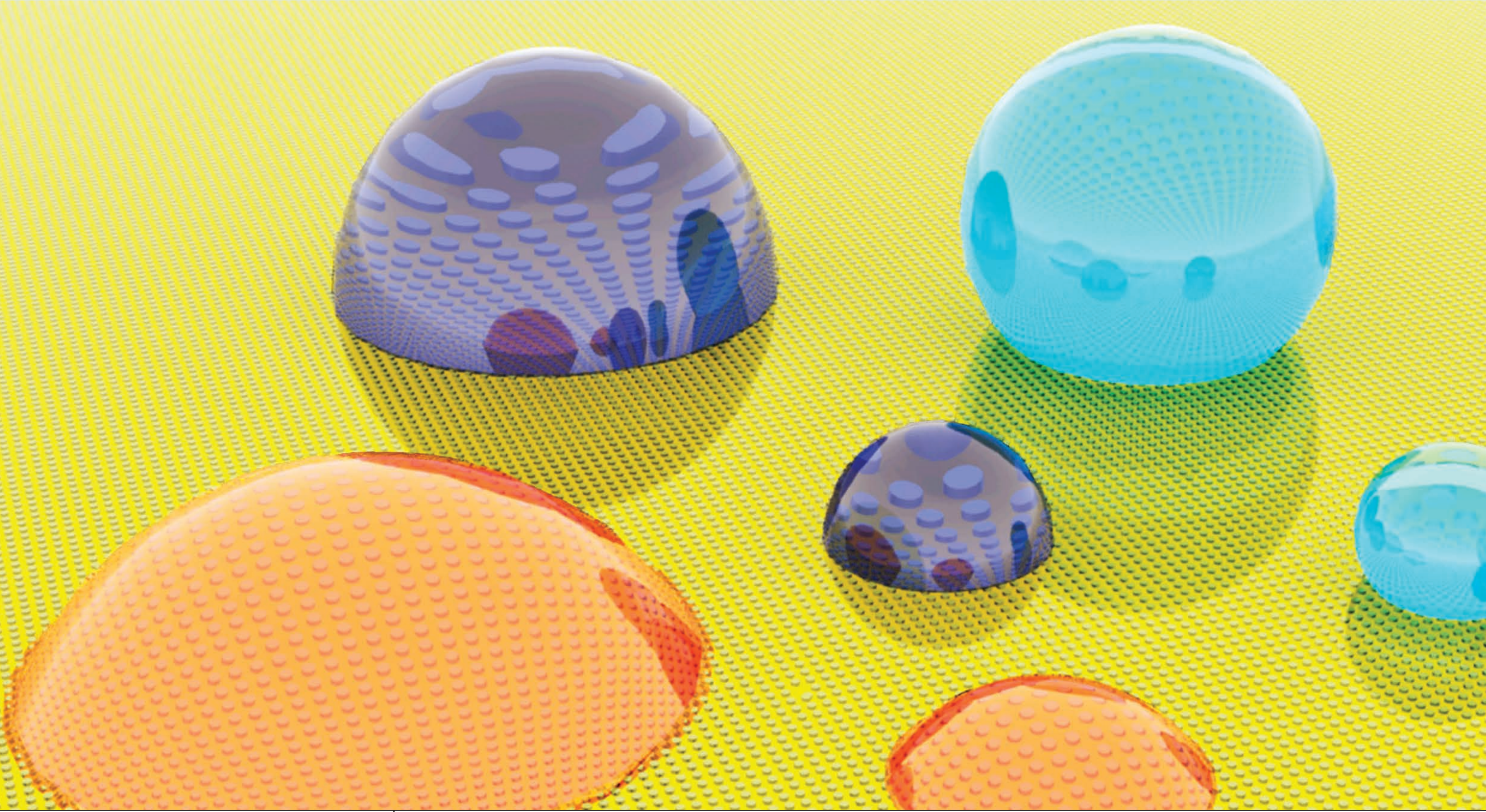
Contact Roman Engel-Herbert at rue2@psu.edu.
For the full story, visit mri.psu.edu/news/

AN ENGINEERED SURFACE UNSTICKS STICKY WATER DROPLETS

The lotus effect has inspired many types of liquid repelling surfaces, but tiny water droplets stick to lotus leaf structures. Now, researchers at Penn State have developed the first nano/micro-textured highly slippery surfaces able to outperform lotus leaf-inspired liquid repellent coatings, particularly in situations where the water is in the form of vapor or tiny droplets.

Enhancing the mobility of liquid droplets on rough surfaces has applications ranging from condensation heat transfer for heat exchangers in power plants to more efficient water harvesting in arid regions where collecting fog droplets on coated meshes provides drinking water and irrigation for agriculture to the prevention of icing and frosting on aircraft wings.

“This represents a fundamentally new concept in engineered surfaces,” said Tak-Sing Wong, assistant professor of mechanical engineering and a faculty member in the Penn State Materials Research Institute. “Our surfaces combine the unique surface architectures



Artist conception of unsticking droplets
Credit: Wong Lab/Penn State

of lotus leaves and pitcher plants, in such a way that these surfaces possess both high surface area and a slippery interface to enhance droplet collection and mobility. Mobility of liquid droplets on rough surfaces is highly dependent on how the liquid wets the surface. We have demonstrated for the first time experimentally that liquid droplets can be highly mobile when in the Wenzel state."

Liquid droplets on rough surfaces come in one of two states, Cassie, in which the liquid partially floats on a layer of air or gas, and Wenzel, in which the droplets are in full contact with the surface, trapping or pinning them. The Wenzel equation was published in 1936 in one of the most highly cited papers in the field; yet until now, it has been extremely challenging to precisely verify the equation experimentally.

In the last decade, tremendous efforts have been devoted to designing rough surfaces that prevent the Cassie-to-Wenzel wetting transition. A key conceptual advance in the current study is that both Cassie and Wenzel state droplets can retain mobility on the slippery rough surface, foregoing the difficult process of preventing the wetting transition.

In order to make Wenzel state droplets mobile, the researchers etched micrometer scale pillars into a silicon surface using photolithography and deep reactive-ion etching, and then created nanoscale textures on the pillars by wet etching. They then infused the nanotextures with a layer of lubricant that completely coated the nanostructures, resulting in greatly reduced pinning of the droplets. The nanostructures also greatly enhanced lubricant retention compared to the microstructured surface alone.

The same design principle can be easily extended to other materials beyond silicon, such as metals, glass, ceramics and plastics. The authors believe this work will open the search for a new, unified model of wetting physics that explains wetting phenomena on rough surfaces such as theirs.

This research was funded by the National Science Foundation CAREER Award and a Graduate Research Fellowship, and the Office of Naval Research (MURI award). The researchers performed their work in the Penn State Nanofabrication Laboratory, part of the National Nanotechnology Infrastructure Network (NNIN), funded by the National Science Foundation. A U.S. provisional patent has been filed for this work.

In addition to Wong, lead author Xianming Dai, postdoctoral scholar Shikuan Yang, and graduate student Birgitt Boschitsch Stogin contributed to the work.

Contact Tak-Sing Wong at tswong@psu.edu.
For the full story, visit mri.psu.edu/news/

Humanitarian
MATERIALS ENGINEERING

Inaugural Humanitarian Materials Awards Announced at Materials Day

UNIVERSITY PARK, Pa. – The winners of the first annual MRI Humanitarian Materials Initiative awards, sponsored by Covestro LLC (formerly Bayer MaterialScience LLC) and the Material Research Institute (MRI), were announced at Materials Day 2015 on the University Park campus.

The MRI Humanitarian Materials Initiative seeks to support ongoing research that is aimed at providing long-term and sustainable solutions to problems in under resourced regions of the world. By bringing world-class materials science and engineering expertise to bear on such issues as materials for clean water and sanitation in remote areas; materials for small-scale, clean electricity generation and storage; low-cost durable and functional shelters; and point-of-care medical technologies, the Penn State Materials Research Institute hopes to attract visionary faculty and students with an interest in transitioning materials technologies to contribute to these real-world issues.

Thirteen faculty-led teams submitted proposals and three winners were chosen.

- **"Moringa-coated sand filters as a sustainable solution to clean water"** is a project led by Stephanie Velegol, instructor in civil and environmental engineering, Manish Kumar, assistant professor of chemical engineering, Michael Erdman, director of Engineering Leadership Development in the College of Engineering, and Bashir Yusuf of Ahmadu Bello University, Nigeria. This ongoing project hopes to improve on the water purifying capability of the seed of the Moringa tree, which grows in equatorial regions around the globe, and can be used as a natural antimicrobial to help clean dirty water. The inventors will use the $15,000 prize to fund four students, undergraduate and graduate, to do research toward improving the Moringa-coated sand filter and for travel to Nigeria to test the training of local residents in the technology. It is estimated that one billion people around the world lack access to clean water.
- **"Thermal stabilization of vaccines for the developing world"** proposed by Melik Demirel, professor of engineering science and mechanics, and including two undergraduate students, would seek to prove the ability to stabilize and preserve biologically active agents used in vaccines, focusing on heat-stable rotavirus vaccine. Rotavirus is a cause of severe diarrhea responsible for the deaths of 600,000 infants and young children each year in developing countries. Based on a novel material, they proposed to obtain superior thermal and mechanical properties in hot and wet environments. The award will provide for viral stabilization research and field testing.
- Also chosen for an award were researchers Jason Williams, head of the Medical Plastics Center of Excellence, and Jonathan Meckley, chair of Plastics Engineering Technology, at Penn State Behrend's School of Engineering. Their project, **"Guatemala roofing panels made from recycled PET,"** would use shredded plastic water and soda bottles to make inexpensive roofing to replace worn out corrugated metal roofing in remote villages in Guatemala. The goal is to create and test a molding process that can be used by the villagers to create their own plastic roofing panels on site. They will design and test an oven capable of using common biomass available nearby, and create procedures for sintering the plastic that will minimize the risk of undersintered panels.

image/bigstock

All of the awards are meant to support undergraduate or graduate researchers and potentially lead to further federal or philanthropic funding.

MRI Director Clive Randall said, “Our initial call for proposals attracted a strong field of candidates, with many more worthy projects than we could fund at this time. We thank Covestro for their generous support. In the future we want to continue and expand on the program. If other corporate sponsors wish to learn more about the MRI Humanitarian Materials Initiative, please contact me or our Industry Relations Manager Dave Fecko.”

About Covestro LLC:

Covestro LLC is one of the leading producers of high-performance polymers in North America and is part of the global Covestro business. Covestro manufactures high-tech polymer materials and develops innovative solutions for products used in many areas of daily life. The main segments served are the automotive, electrical and electronics, construction and sports and leisure industries. The Covestro group has 30 production sites around the globe and employed approximately 14,200 people at the end of 2014. Covestro is a Bayer Group company.

MRI Seeks Partners for Humanitarian Materials Engineering

The Materials Research Institute, which coordinates interdisciplinary materials related research at Penn State, is actively expanding its humanitarian materials engineering initiative with strategic partners within the University and beyond.

Humanitarian Materials Engineering offers new opportunities in the education of our students to think beyond typical problems, but also provides solutions under the traditional strategies of structure-property-processing-performance approaches. These solutions can impact the major issues of global health and stewardship of natural resources, including clean water, food security, and energy availability for millions of people around the globe. We believe that materials science and engineering is an approach highly relevant to humanitarian engineering, applying materials principles in systems that are sustainable in terms of cost, local availability, repair strategies, robustness to degradation in extreme natural environments, and cultural considerations.

It is our vision to apply both the depth and breadth of our collective expertise to engage in research without boundaries, enable the transition of materials research into society, and aid in the development of a new generation of highly qualified graduates who can both communicate and innovate in a converging world. The overall mission is summarized in an ambitious philosophical statement that reflects our

Humanitarian
MATERIALS ENGINEERING

total organization: MRI supports scientific excellence, technology leadership, and the education of a new generation of globally conscious materials scientists and engineers capable of solving the grand challenges of the 21st century.

MRI plans to support the development of humanitarian materials engineering in the following ways:

(a) Develop a Humanitarian Materials Characterization and Testing Laboratory within the Materials Characterization Laboratory, dedicated to testing indigenous material for humanitarian engineering programs through testing the environmental aging effects on materials in high ultraviolet radiation, high humidity, large thermal cycles, and abrasive wear from particulates

(b) Seed fund humanitarian materials design projects with faculty and students

(c) Co-hire at least one faculty within this field, possibly in conjunction with the College of Arts and Architecture and/or another school or department

(d) Highlight faculty activities and success stories on humanitarian materials programs on the MRI webpage and in *Focus on Materials* quarterly bulletin

(e) Form joint project initiatives with different branch campuses, departments, institutes, and organizations within Penn State

(f) Expand our broader impacts within this humanitarian materials philosophy to NSF programs

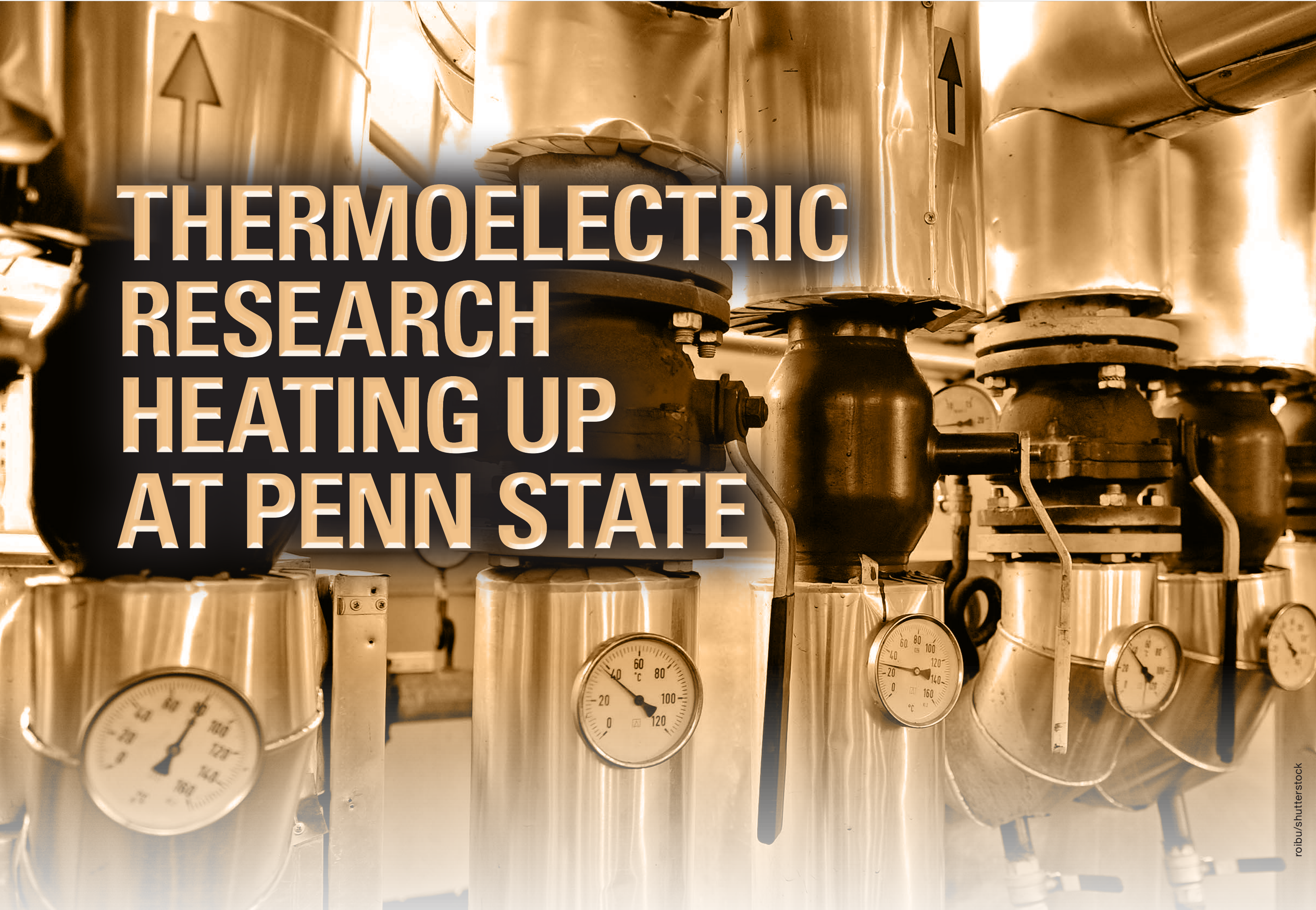
(g) Engage with peer research organizations in developing countries in partnership with Global Engagement Network (GEN) under the University's Office of Global Programs

(h) Obtain foundation, government, crowd-funding, and corporate support to aid MRI's humanitarian materials projects

(i) Run the first international conference on humanitarian materials science, led by Penn State University – possibly in partnership with a GEN member – within the next 3 years

(j) Subsidize faculty/student travel to MRS-Africa to represent PSU/MRI materials effort and to explore networking.

If you would be interested in partnering with MRI on this ambitious program, contact director Clive Randall (car4@psu.edu) or industrial relations coordinator Dave Fecko (dlf5023@psu.edu, 814 865-6691).



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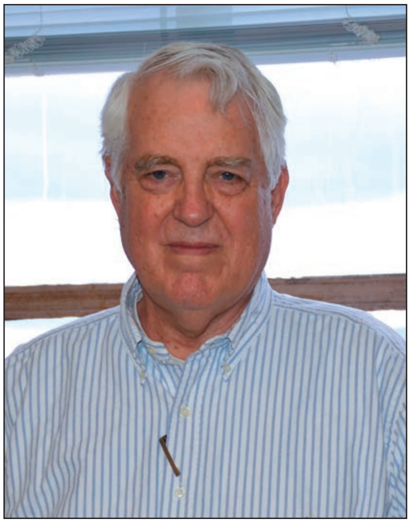
THERMOELECTRIC RESEARCH HEATING UP AT PENN STATE

Thermoelectric materials have the ability to turn heat into electricity. Long used in niche applications such as providing electrical energy on long distance spaceflights or as refrigeration in portable coolers, thermoelectrics are beginning to find more prominent applications as their performance improves.

Thermoelectric materials have the potential to utilize the vast amounts of waste heat lost to the environment through industrial processes. The Department of Energy estimates that between 5-13 quadrillion BTUs of energy a year are generated by waste heat, enough to power some two million homes. Even capturing a portion of that heat to generate electricity could save companies an estimated 5 percent in energy costs. In vehicles, a thermoelectric device to capture and convert exhaust heat could eliminate the need for an alternator.

The field of thermoelectrics and thermally functional materials was a backwater of research at Penn State and other research universities for most of the past 50 years, stalled by a failure to develop new materials with improved functionality. But in the last decade, new materials with improved thermoelectric efficiency have reinvigorated the search for functional thermal materials and devices, making this one of the emerging research fields for Penn State and the broader materials community.

The thermoelectric effect has been known for generations. The German physicist Thomas Johann Seebeck discovered thermoelectricity in the 1820s when he discovered that two metals with differing temperatures at their junction could deflect a magnet. It was later realized that the temperature difference was actually producing an electrical current. The Seebeck effect is defined as the electrical potential produced by a temperature difference. Since Seebeck's time, the connection between heat and electric current has been put to use to scavenge useful electricity from waste heat, or reversing the effect and applying an electric current to a thermally functional material, to produce heating or cooling, a process called the Peltier effect. Penn State researchers are pursuing both paths.



Prof. Jerry Mahan

In 1996, one of the more cited papers in the field of thermoelectrics was published by two Penn State physicists, Jerry Mahan and his onetime post-doc and current colleague Jorge Sofo. Mahan is a theoretical physicist who along with his university post spent 30 years consulting for the General Electric Research Lab, primarily modeling devices, including thermal devices. Their paper was about figuring out what the best thermoelectric material would look like if it could be designed perfectly, a forerunner of the current Materials Genome Project, which is an attempt to cut down the time it takes to produce useful materials by using computational techniques.

"The most generally useful materials have to have three properties: one is low electrical resistance; another is low thermal conductivity; the third is a very high Seebeck coefficient," Mahan explained. "We said if you want to have the perfect material, it has to have these properties. And then people tried to find those materials. It has led people in the right direction using the Mahan-Sofo algorithm.

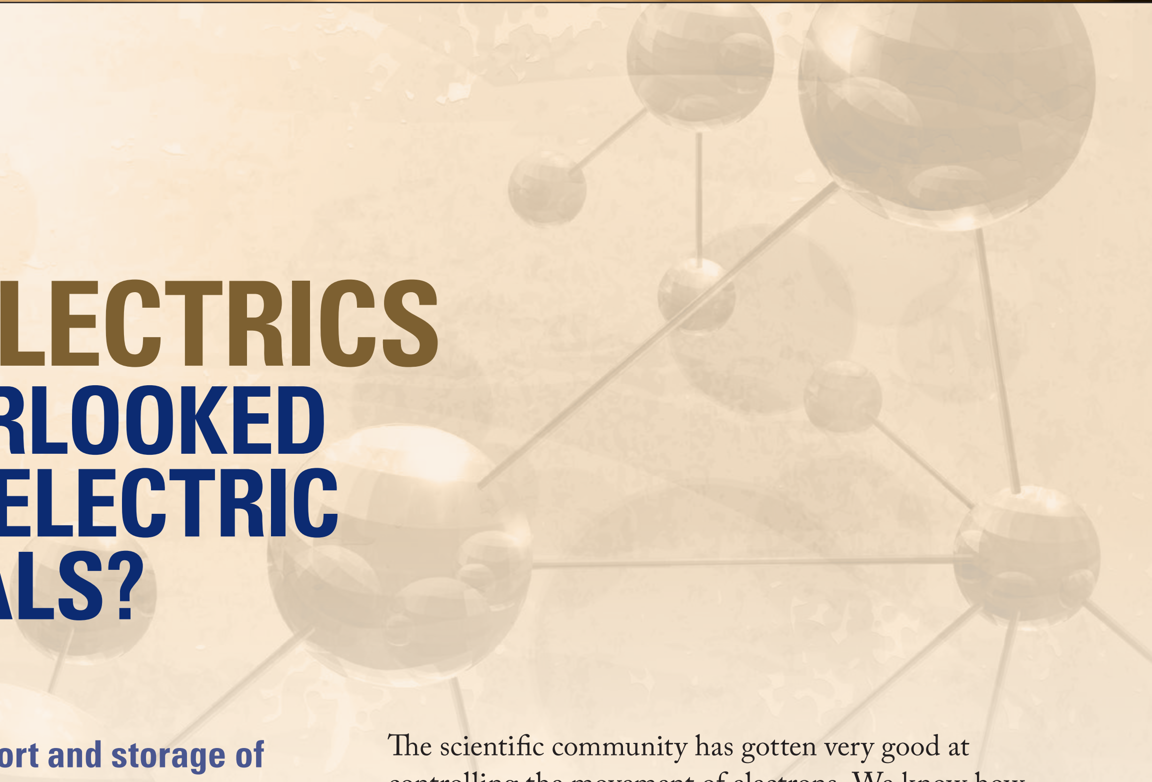
"The field of thermoelectrics has blossomed in the last few years with the advances in power conversion materials," Mahan added. "We've found good high temperature materials, good for waste heat power generation. Now the great need is for materials that work at room temperature or below. All my theoretical work has never found a reason why you couldn't have one. Someday someone will stumble across a material and the field will take off."

The figure of merit for comparison of the properties Mahan discussed is called zT.

Jorge Sofo, professor of physics and professor of materials science and engineering, said, "You could say that at the beginning in the early 1950s, the best materials had a zT just below 1. Now we are at 1.1 and what we need is 4. If you go above 2 with that number at room temperature, you can start to get real life applications. At 4, thermoelectrics would be everywhere."

Sofo explained that the standard device hasn't changed since Abraham Iofe developed the first semiconductor thermoelectric device in 1953. The device is always a negative semiconductor that carries electrons and a positive semiconductor that carries holes. In an n-type semiconductor the electrical current and heat current travel in the same direction. In a p-type semiconductor, the electrical current and heat current go in opposite directions. Hook them up and you have a thermoelectric device. The design hasn't changed in 60 years, so what is needed is a material with a seriously higher zT.

That material may have been discovered here at Penn State, or at least that's what Mahan thinks. "When I saw Clive Randall's data, I said, 'That's spectacular, I hope you patented it.' The material is strontium-barium niobate. It's an alloy with a very complicated crystal structure. It's the type of solid we didn't know about in 1955."



ARE FERROELECTRICS THE OVERLOOKED THERMOELECTRIC MATERIALS?

Controlling the transport and storage of thermal energy could potentially have a powerful impact on our lives. After all, everything you can think of has thermal energy. Atoms vibrate, molecules collide, heat energy radiates from the sun in the form of light waves. We use heat to create electricity through the phase change of water into steam in power plants.

The scientific community has gotten very good at controlling the movement of electrons. We know how to make materials that slow their movement, that store their energy, and redistribute electrons at electrodes to do work in slow batteries or fast capacitors. But are there other classes of materials we could use to control heat much as we can control electrons? The answer might be a type of material that we have overlooked, a class of materials called ferroelectrics.

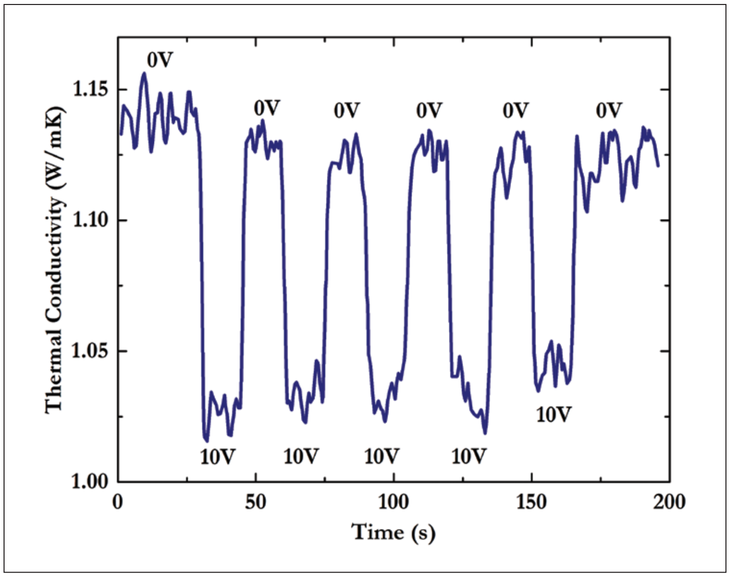
Penn State is widely known for the study of ferroelectrics, a class of crystalline materials that shows a spontaneous electric polarization that can be reversed when an electric field is applied. Ferroelectric materials are used for nonvolatile memory in computers, in pyroelectric applications for infrared sensing, and in piezoelectric applications such as sensors and capacitors, of which trillions are produced every year.

Clive Randall is one of the scientists who studies ferroelectrics at Penn State, following in the footsteps of a long line of highly regarded researchers and teachers who have made Penn State a leading center for ferroelectrics and the larger class of materials called piezoelectrics – materials that develop an electric charge in response to mechanical stress – and pyroelectrics – materials that develop an electric charge as a result of a change in temperature.

image/bigstock

Ferroelectricity is analogous to ferromagnetism, which is used to read and write data in digital electronics. Where magnets have north and south magnetic poles, which can be flipped to store the zeroes and ones of binary information, ferroelectrics have coupled positive and negative charges that form dipoles that can also be collectively flipped. The two most commonly used ferroelectrics are barium titanate and lead zirconium titanate (PZT). Both of these materials were discovered more than 60 years ago, and belong to the perovskite family – a related material $SrTiO_3$ is one of the highest performing thermoelectrics.

Several years ago, Randall began to wonder if there might be some way to use the deep knowledge they had gained about ferroelectric materials and apply it to the control of heat energy. Looking through some of the classic works on ferroelectricity, he was surprised to find that the telluride family of materials was among those listed as ferroelectrics.



Electrically driven thermal switch. The thermal conductivity is modulated by electric field control of the ferroelectric domain structure in lead zirconate titanate films. Credit: Trolier-McKinstry Lab

"It didn't seem appropriate," he said of his revelation. "Usually, ferroelectrics are applied to insulators when you want to minimize electrical conduction. But a good thermal material has high electron conductivity, like a metal. When ferroelectrics become highly conductive, it destabilizes the long range dipolar ordering necessary for ferroelectricity. Is it even possible to have a metallic ferroelectric?"

There were little clues in the classic textbooks that hinted that the telluride materials had the kind of crystal symmetries that were consistent with ferroelectricity, but because they had such high electrical conductivity, they couldn't switch polarization, a requirement of true ferroelectrics.

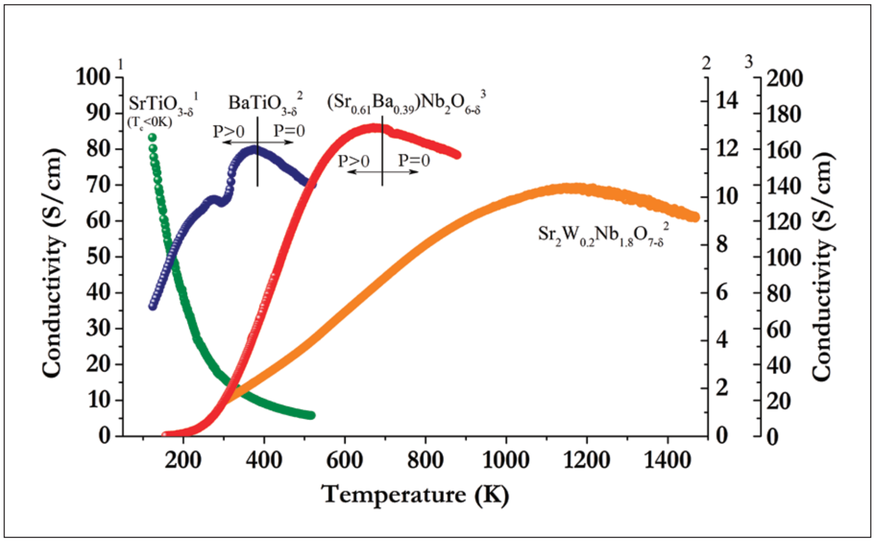
But, he reasoned, if a good thermoelectric material had some of the characteristics of a ferroelectric, wasn't that a good enough path to follow to explore this new, unknown territory? Randall thought it was.

The figure of merit that indicates the strength of thermoelectricity in a material is known as zT. It consists of three elements: a high Seebeck coefficient (a thermal gradient across a sample creates a voltage), high electrical transport, and very low thermal transport. One of the problems with finding materials with high zT is that good conductors of electricity are usually good conductors of heat. If you have ever burned your hand on a frying pan, you know that metals are good conductors of heat, and metals also have lots of free electrons, making them good electrical conductors. Ferroelectrics, which are insulators, are poor conductors of electrons, but also have low thermal transport. This is because the packets of heat energy called phonons scatter off the internal polar nanostructures of ferroelectrics, which slows the spread of heat from the hot side to the colder side of a material; developing a phonon glass, within the crystal structure.

"We started asking very fundamental questions about the nature of ferroelectricity in highly conductive materials. If there were such a thing as a metallic ferroelectric, could it have the high electrical conductivity and low thermal conductivity required for high zT? And how were the conductivity and the Seebeck coefficient being influenced by the phase transition behavior of a number of ferroelectric type materials," Randall recalled.

Phase transitions are the changes in the properties or structure of a material that take place as heat energy is added or removed from the system. Randall and his team found that in many of these ferroelectric crystals at around the phase transition point a transition in the freedom of electron movement occurred from semiconductor to metallic, from low conductivity to high conductivity.

"We've seen this transition in a number of ferroelectric materials at over 1000 Kelvin (1340 °F). As we asked these basic questions about the interrelationship between thermal electricity and ferroelectricity, we turned up some very promising materials, such as the tungsten bronzes," Randall said. In September 2014, his initial results were published in a journal article in *Physics Review B* with coauthors Jonathan Bock, Susan Trolier-McKinstry, and Gerald Mahan.



Comparative study of temperature dependences of conductivity for various ferroelectric and related oxide materials that have been reduced to have high levels of oxygen vacancy non-stoichiometry. The presence of ferroelectric phase transitions between 0 Kelvin to above 1000 Kelvin across different crystal structures and compositions enables control of the crossover between semiconducting behavior to metallic-like conduction. Credit: Randall Lab

Applications: Cooling circuits, cooling buildings

Crystal grain size in a ferroelectric material can have a profound effect on thermal transport. In ferroelectrics, a region of material called a domain has a uniform magnetic polarization – the north/south poles point in the same direction rather than randomly. By switching the polarity of domains with an electric field, not only is the polarization controlled, but thermal transport can be manipulated as well. This could lead to the ability to turn thermal transport on and off like a pump. This could be useful for applications such as heating or cooling circuits in power electronics where the circuits operate most efficiently at a certain temperature. If the circuit gets too hot, thermal conduction is turned on with an electric field. If it is cooling down too much, thermal conduction could be turned off.

There are numerous opportunities for utilizing thermal control, from the very small in microelectronics to the very large in building materials that buffer large thermal fluctuations and keep interior spaces at a uniform temperature or lower the cost of heating and cooling.

"We hope this approach using ferroelectrics will spur a whole new area of research for materials," Randall said.

At Penn State, Randall's group specializes in bulk single crystal and polycrystalline materials, while Susan Trolier-McKinstry's group specializes in thin film materials for thermal control. Other collaborators include Patrick Hopkins at the University of Virginia, and former Penn State post-doc John Ifeld, now at Sandia National Labs. Trolier-McKinstry is currently the co-director of the Center for Dielectrics and Piezoelectrics, a joint industry/university cooperative research center with North Carolina State University sponsored by the National Science Foundation. UVA and Sandia are also CDP members.

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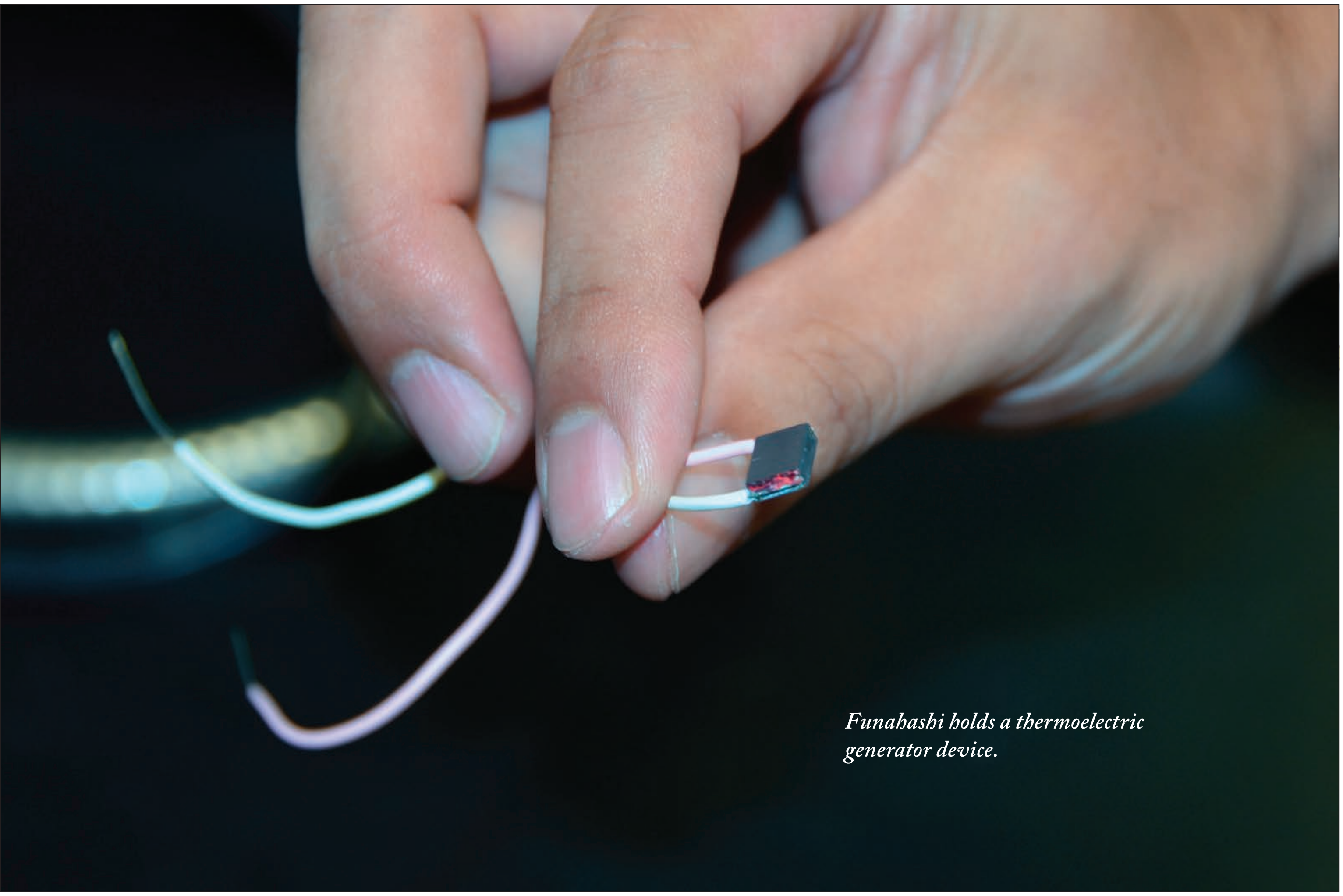
A JAPANESE ENGINEER IS MAKING THERMOELECTRIC DEVICES AT PENN STATE

Visiting engineer Shuichi Funahashi in the dielectrics lab in the Millennium Science Complex

"I have to produce the next generation of thermoelectric devices for my company," Shuichi Funahashi, an engineer from the giant electronic device manufacturer Murata Manufacturing Company, told me. Mr. Funahashi is visiting Penn State and MRI on a two-year research mission, tasked with finding new materials and devices to keep his company at the forefront of their industry. Murata sends young engineers to work with MRI researchers on a recurring basis. The relationship between Murata and the Center for Dielectric Studies, now the Center for Dielectrics and Piezoelectrics, based at NC State and Penn State, goes back many years.

"I focus on the materials, but the company has a broader program. Right now I am focusing on phonon mechanisms to improve materials and expand thermoelectric applications as a power source for wireless sensors," he said. "Basically, thermoelectric materials will be used for heat recovery, but it is too early for companies to bring those to market. But in a small battery, the materials can be very useful."

Shuichi is working with Clive Randall's group on an oxide with low thermal conductivity. Oxides are not generally used as a thermoelectric material, but the results of their research seem promising enough to think they might improve the thermoelectric properties considerably, he said.



Funahashi holds a thermoelectric generator device.

I asked him how he was getting along here in the U.S. and he responded enthusiastically. “Of course, I do like it here. I like nature and this atmosphere. Everyone is very kind.”

Amanda Baker, an MRI staff engineer in Randall’s group, helps him make his samples, and the microscopy staff helps with the electron microscope work. His devices incorporate the metal-oxide materials into multilayer ceramic capacitor technology in order to make thermoelectric generators. When he returns to Japan after his tour in the U.S., Shuichi hopes to continue his research on thermoelectric materials until his company has a world-leading product. In the meantime, he is keeping his eyes open for any new technologies Murata might turn into products.

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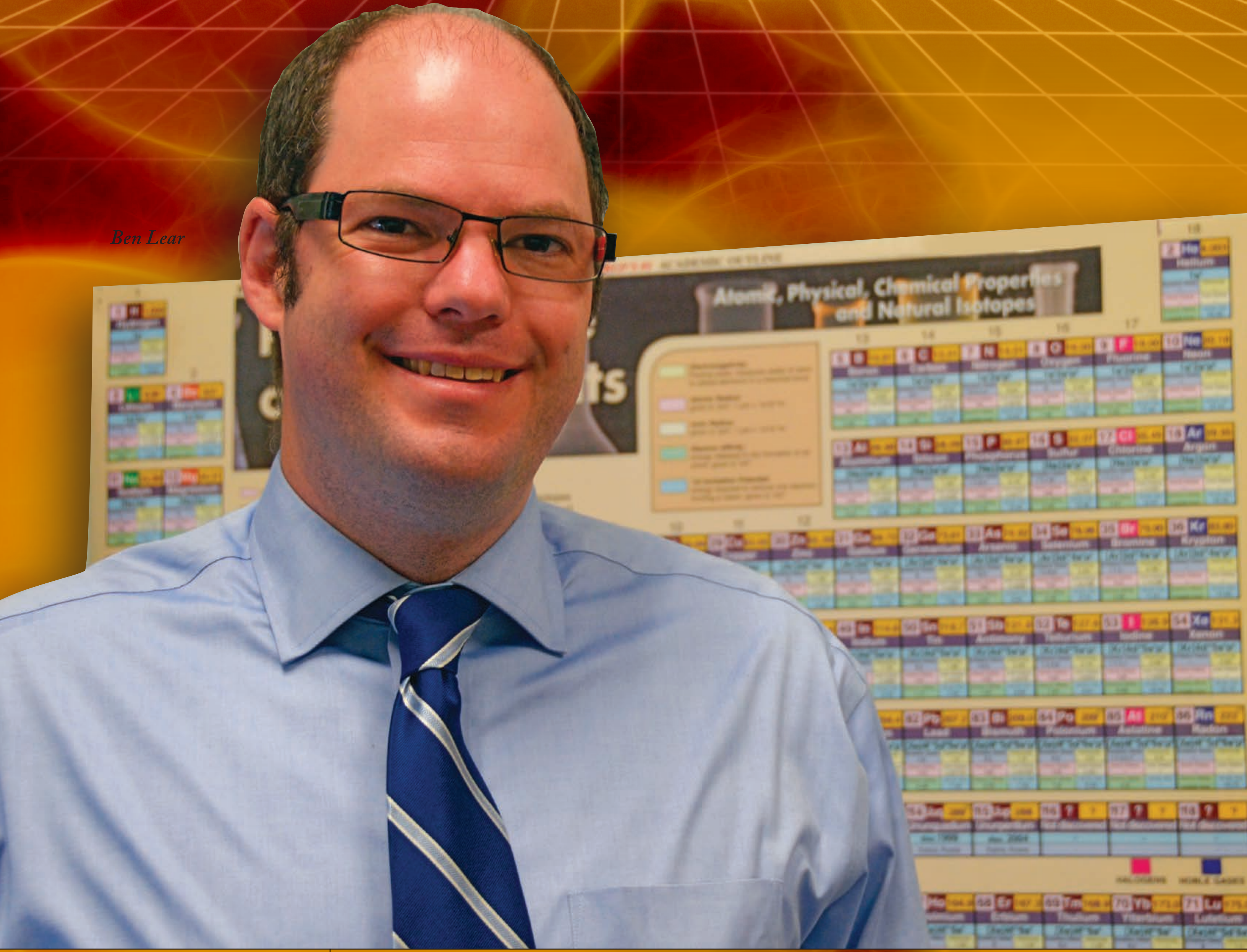
ABSORBING HEAT



Ben Lear

The control of heat at the nanoscale provides interesting possibilities for moving heat from locations where it is not wanted, or for using the buildup of heat in nanoparticles to drive chemical reactions more efficiently.

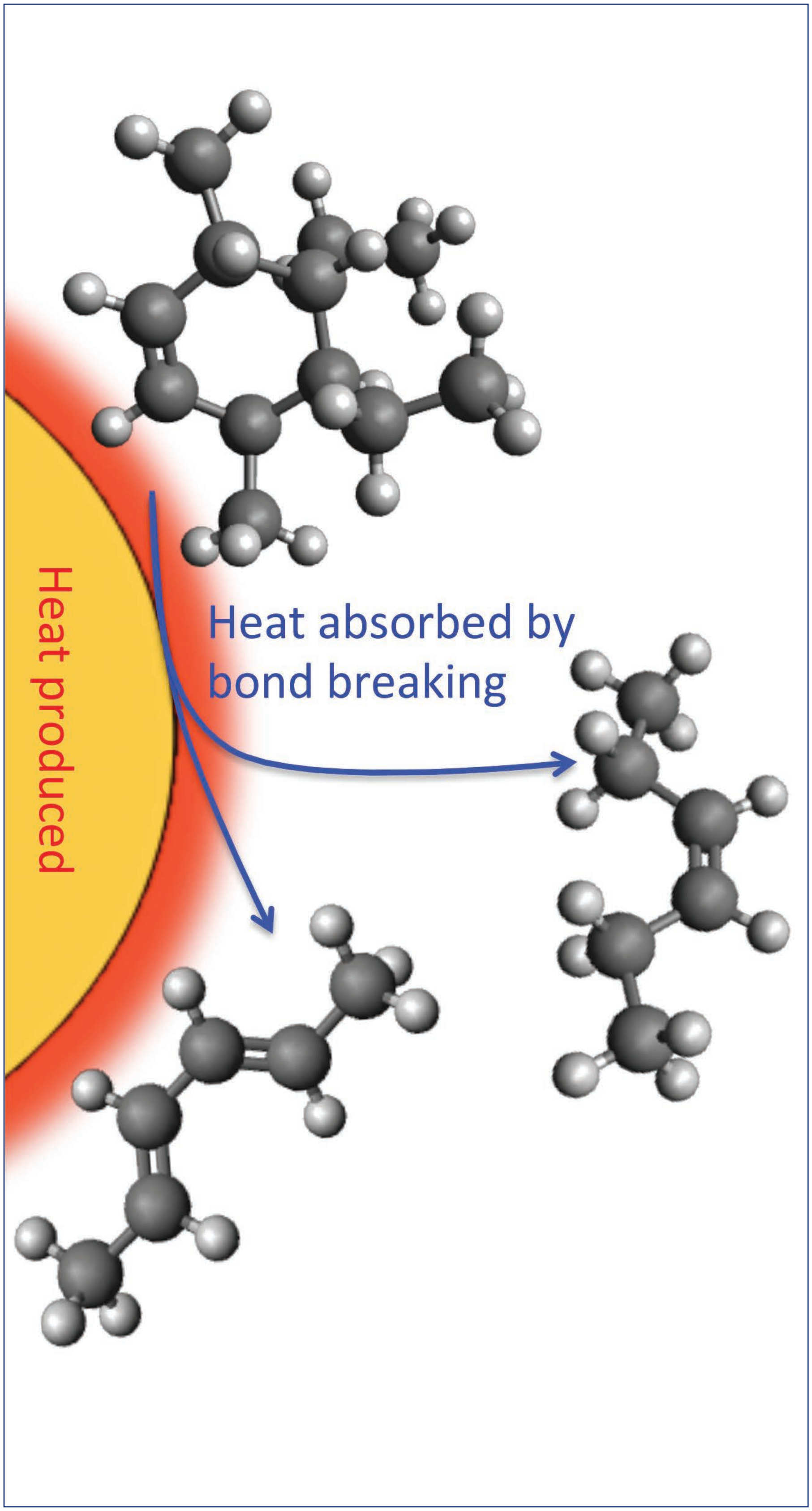
The Lear group in the Department of Chemistry has a long-standing program that looks at photothermal heating of nanoparticles – nanoparticles that absorb light strongly, and then efficiently converts this light to heat. As the thermal energy builds up, it is dissipated into the local environment, where it can drive catalytic reactions, ablate cancer cells, or decompose polymers.

In the process of studying this behavior of nanoparticles, they observed that driving reactions that absorbed heat resulted in more efficient cooling of the particles. “That got us thinking that maybe we could use those endothermic or heat absorbing reactions to function as heat sinks,” said Ben Lear, assistant professor of chemistry. Lear wrote a proposal to explore that possibility, and the Air Force funded his group to study the possibility of using the endothermic process to cool equipment such as lasers that require absorbing huge amounts of heat on a rapid time scale. “When you think about ways to absorb heat, you usually get either things that are water cooled or air cooled,” Lear continued. “You have a computer and you use a fan to blow cold air over it. It turns out the heat absorbing power of air is pretty poor.”

Likewise, car engines are cooled by water circulating from a radiator. The thermal conductivity is better, but the heat absorbing power is still poor. Water can only absorb a limited amount of heat before it boils. The real cooling comes from a phase change, such as a liquid to gas transition as in the evaporation of liquid nitrogen. The amount of energy that’s necessary to undergo a phase change is significantly higher than the amount of energy needed to heat up or cool a material, Lear noted. The reason for the higher energy requirement for evaporation is the attractive force between molecules is strong in liquids. It’s what holds them together. With enough energy in the system, the molecules will finally start moving fast enough to fly apart.

The attractive force holding two atoms together in a chemical bond is 10 to100 times stronger than the attractive force between molecules. They speculated that using the force of chemical bonds to absorb heat would increase the heat absorbing power by at least 10 times. In addition, the timescales associated with breaking chemical bonds are advantageous. A laser, such as the kind the Air Force would put on a plane’s detection systems, generates large amounts of heat as it creates laser pulses in the femtosecond timescale (one quadrillionth of a second). This creates a problem for using a liquid-to-gas absorption method, because that process takes place at a nanosecond time scale, a million times slower. Chemical bonds can break at a picosecond timescale (one trillionth of a second), so they are far closer to the speed of the laser pulses and the heat they are producing.

“What we would like to do is create a reactive cooling bath that has a lot of cooling power built into it. One where we can tune the temperature so that you can run systems at their most efficient temperature,” said Lear.



This would be useful for industry applications, where they would like to be able to hold a machine at a given temperature for long periods. By selecting an appropriate chemical bond, the desired temperature can be maintained. Ideally, the chemical reaction would be reversible – the atomic bonds would break apart, the resulting chemical could be moved to a cooler place and the bonds reformed. It would also be ideal if the chemical was not caustic in either phase. Although it is not a strict requirement, it would also be easier to work with a chemical that is in a liquid form at the desired temperature, so it can be pumped through the cooling system.

The researchers plan to start with a set of well-known endothermic reactions known as Diels-Alder reactions. These reactions are simple to run, reversible, and can be made from oil-like molecules. "This is something we are used to using with metal systems, and it is non-reacting. Pick the right kinds of oils and whether the bond is broken or not, it will remain an oil in either case, and oils are something that we are already comfortable using around metallic and electronic components, Lear concluded."

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FULFILLING THE LONG-DELAYED PROMISE OF SOLID STATE REFRIGERATION

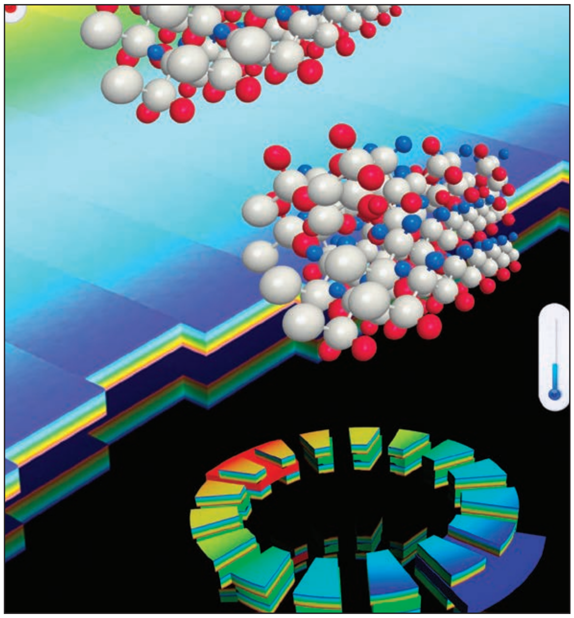
Prof. Qiming Zhang (L) with Ph.D. student Tian Zhang (M) and post-doc Xiaoshi Qian (R) with a prototype device

In Russia just after the Second World War, in what is now St. Petersburg, a physicist named Abram Ioffe pointed out that thermoelectric materials could be used to make a solid state refrigerator with no moving parts. This ignited a worldwide research frenzy, according to Penn State theoretical physicist Jerry Mahan.

Major labs around the world, including General Electric, Philips in Holland, Westinghouse, Bell, RCA, and IBM, all got busy and measured every known material. Although there were many niche applications, for instance for small, portable coolers or for silent-running refrigeration aboard the space station, those researchers never found a material efficient enough at cooling to replace the refrigerator in your kitchen, Mahan said. The most popular thermoelectric material, bismuth telluride, has been used commercially for 60 years in applications that required reliability and compact size more than efficiency. It's still used today.

It was not until the 1990s that funding agencies again began to look into solid state refrigeration. The renewed interest arose from new combinations of materials made out of as many as three, four, or even five different elements, widening the search for better electrocaloric materials. In 2004, based on thermodynamic theory and molecular structure consideration, Penn State electrical engineer Qiming Zhang predicted a temperate change of more than 15 K in polymer films, at temperatures near 100 degree C. In 2006, a thin-film perovskite material was shown to produce a temperature change of 10 K, about 10X higher than previous materials, but at temperatures above 200 degrees C.

Theorists, including Mahan, have doubts that an electrocaloric device will ever be able to equal the efficiency of the household refrigerator that relies on the compression of gases, but experimentalists continue to look for (and find) better and better materials. One of those leading the hunt is Penn State's Qiming Zhang, recognized as one of the world leaders in electrocaloric materials.



Schematic of the EC device (bottom) with the molecular structure of the material (white/blue/red atoms).

"I would have to disagree with the theorists," Zhang remarks. "When you compare the mechanical loss from a typical refrigerator, an electrical field is so much easier to apply than mechanical force. You have to use electricity to drive the motor and the motor compresses the air. In solid state refrigeration, you apply an electric field directly to the refrigerant and change the temperature. You eliminate the middle stage."

Plus, he says, you can make use of something called the regeneration process. When the refrigerant changes from a hot to a cold temperature it will release heat. When the opposite effect occurs and the refrigerant changes from cold to hot, the released heat can be used to heat another process, which will save energy.

In 2008, Zhang showed that a large electrocaloric effect could be realized at room temperature in a ferroic polymer with a temperature change of 12 degrees C. Ferroic polymers are ones that show a spontaneous electrical polarization.

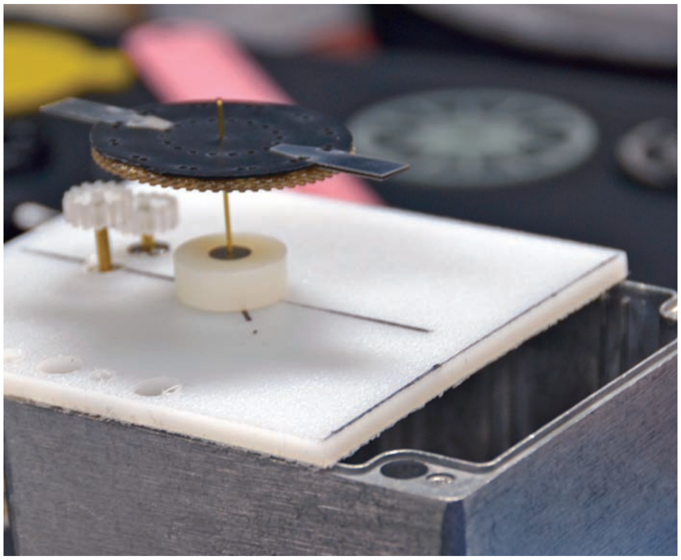
Some background

In ferroic materials there are units of charge called dipoles that are linked to the lattice structure of the material. A change to the lattice can create an electric charge and the addition of charge can change the structure of the material. This is the basis of piezoelectricity, the familiar property used in ultrasound imaging. Some materials also have a spontaneous electrical polarization based on changes of temperature. This is the pyroelectric effect, used in night vision glasses

"In a good electrocaloric material you have a lot of random dipoles (molecules with separate positive and negative charge). When you add an electric field, the dipoles line up. You can use this process to cool or heat things," says Zhang. "It is something like what happens when fluid becomes solid. It goes from a random structure to a crystal structure."

For a long time, people didn't pay much attention to the disordered state of the dipoles but instead were looking for materials that had high long-range polarity. It turns out that a very disordered material that can be induced into order quickly is a key to a large electrocaloric effect. Another way to put it is that the material should have a low dielectric constant; that is, a low capacity to hold opposite charges. Polymers have a lower dielectric constant than ceramics, such as barium tatinate. They also have a higher breakdown strength than ceramics.

"The same concept can be applied to looking for ceramics that could be good electrocaloric materials," Zhang offers. "By combining those two things, a low dielectric constant and a high breakdown field, you can modify the ceramics to make good electrocalorics."



A close-up of the prototype to demonstrate the electrocaloric effect

Zhang's own research on electrocalorics covers three fields – polymers, ceramics, and a combination of the two called ceramic-polymer composites that can combine the best features of the other two types of material. Right now the biggest advantage to ceramics is that there are multilayer ceramic manufacturing technologies available that are well understood and inexpensive. For that reason, Zhang expects to see ceramic electrocaloric devices reach the marketplace first, though he believes it will take time and resources to reach a point where solid state refrigeration replaces today's vapor compression cooling.

"A lot of people still question if this will work out. The giant magnetocaloric effect (involving magnetic materials) was discovered in the 1990s, and a few years ago, they have demonstrated a working device. For electrocaloric cooling, there is still no working device. Right now, we just want to make a simple working electrocaloric cooling device we can set on a table and run with a battery or power from a wall outlet."

Zhang compares the current state of electrocaloric devices to the early stages of liquid crystal displays, which were developed in the 1980s. At first the liquid crystals were slow and only useful for handheld calculators. When they were first tried on television screens, colors disappeared if you shifted your viewing angle. Now, huge flat screen panels using liquid crystals are common. Electrocaloric materials are like that, he believes.

"If we can design a material properly, the way they did with liquid crystals, I think we would have something. From the basic material and device point of view, I think that electrocaloric cooling is the future."

If Zhang is right, it will be because solid state refrigeration requires no compressor that can be bulky and heavy, and no greenhouse gases that can leak into the atmosphere. If they could replace all air conditioning and refrigeration, they would be tapping into a 100 billion dollar industry. For now, he is envisioning compact personal air conditioners that would be useful if they could change the temperature of the surrounding by 10 degrees or less. Another idea, which he is discussing with the National Renewable Energy Laboratory, is to use compact solid state air conditioners for use in the sleeping cabs of long-distance trucks so that they can turn off their engines when they sleep, thereby saving huge amounts of diesel fuel.

"Once we demonstrate something that's useful, we can capture the interest of many companies," Zhang says. "The overall consensus of the electrocaloric research community is that we really need to put a device on the table and let people put their hands on it to feel significant cooling power."

This fall (before December), Zhang will received funding of just under $3 million from DARPA, the agency for futuristic devices for the military, to fund a project to integrate electrocaloric materials with thermoelectric materials for a hybrid solid state cooling system.

"Our goal is to produce a product in two to three years," he says optimistically.

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AMAN HAQUE'S POWERFUL LAB IS THE SIZE OF A FINGERTIP

Aman Haque likes a challenge, and understanding thermal transport at the nanoscale is unexplored territory with plenty of room for experimental discovery. The professor of mechanical engineering is one of only a handful of researchers around the world with the capability to study the thermal and electrical properties of a material in real time under an electron microscope. He does it with a laboratory small enough to sit on a fingertip.

Aman Haque with visiting Ph.D. student Qian Zhang

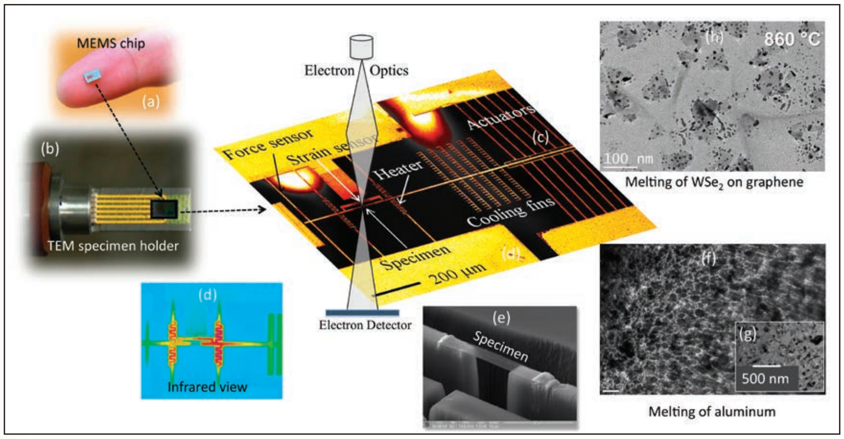
Haque shrinks the test facilities that fit into a full scale lab onto a microchip – including sensors, actuators, heaters and cooling fans, thermal and electronic measurement devices, a tensile testing tool, and the microelectronics to make them all work. This laboratory is small enough to fit into the specimen holder of a transmission electron microscope such as the state of the art Titan, housed in the Materials Research Institute's microscopy facilities. "My expertise is developing experimental set-ups," said Haque. "I am interested in doing very fundamental scientific experiments at the length scale where these experiments are difficult to do."

Haque and his students look at how heat transfers in ultrathin films.

"People are trying to capture the awesome properties of nanoscale materials so that we can use them at the bulk level," said Haque, whose name is pronounced like the bird of prey. "But that application of nanoscale materials is still at the laboratory level."

There is, however, one place where nanoscale materials are already in use: in the microelectronics industry and the shrinking world of cell phones and computers. Haque collaborates with Intel, the giant computer chip manufacturer, to study how heat moves in the materials, such as low-K oxides, that Intel uses in its computer chips. His group also works on a phenomenon called interfacial thermal resistance (ITR), which is one of the dominant factors affecting thermal transport when materials shrink to the nanoscale. In microelectronics, the ability to dissipate heat is crucial, and materials with high ITR are poor conductors of heat due to scattering of phonons and electrons at the point that two different materials meet. This phenomenon is one of the most difficult properties to measure at the nanoscale, Haque said, so his group is developing new techniques to observe ITR under the microscope.

“In the 1970s, nobody thought that heat transfer would be a problem for computer engineers. Even in the eighties and nineties we could have a fan in a computer and it would cool well enough. But these days, if you are looking at high performance computer chips, you cannot cool computers with fans anymore,” Haque explained. This is where a nanoscale material could have immediate applications, Haque said. You could think of a nanoscale material that could go into nanoscale devices for applications like cooling transistors.



(a) A nanofabricated chip with mechanical, thermal and electrical probing capabilities (b) mounted on a TEM specimen holder (c) to allow ‘see’ microstructures and defects while measuring properties (d) infrared image of heaters (e) SEM image of specimen, (f) melting of aluminum (g) aluminum at room temperature (h) melting of WSe2 on graphene Credit: Haque Lab

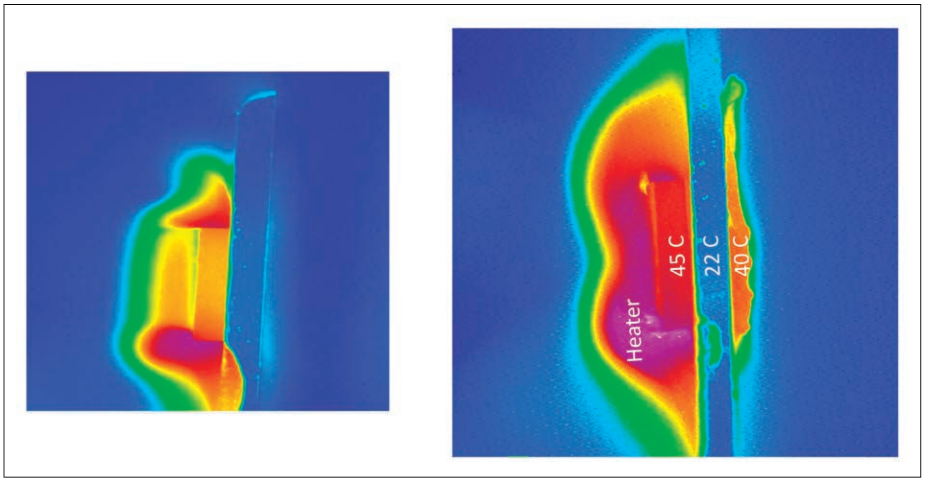
In fact, that may be just the kind of material Haque has developed. Although details are still confidential due to intellectual property concerns, he believes that he has discovered a material with ballistic transport properties. That means that the heat conductors, packets of heat energy called phonons, pass at high speed through the material without scattering or heating up the material. The material remains at room temperature as it dissipates heat from a source, in this case a heater but potentially a computer chip, into a heat sink. Think of it as room temperature superconductivity, but with phonons instead of electrons.

“This is a very old idea, but people have been doing it at very low temperature, as low as 4 Kelvin. At that low temperature there is very little scattering. We are seeing ballistic heat transfer not at 4 K but at 300 K, room temperature. Because there is no scattering, the material will transfer huge amounts of heat without getting heated at all. Batteries are also sensitive to temperature. People are trying to get very high energy density batteries, and it’s the same with electronics. Anywhere people are dealing with energy they will want either a good conductor or a poor conductor of thermal energy.”

What can you do with a lab on a chip?

A miniaturized lab that can be inserted into the sample holder of a TEM opens up possibilities that previously could only be understood through simulation and mathematical modeling. In the TEM, he can see defects in a material that can affect the material’s thermal, electronic, and mechanical properties. Those properties can be tested when particular dopants are added. He can watch in real time as a crystalline material becomes amorphous as he adds heat.

“These are unique research capabilities where you can see what is happening inside a material as you



Ballistic (scatter free) phonon transport at room temperature. The 0.5 mm thick material remains at room temperature, while transporting heat from the heater to the sample. *Credit: Haque Lab*

pass current, as you pass heat, as you transmit load. There is no guessing. This automatically connects experiment to theory. Because the theory people see what is happening, the theory they come up with is accurate and fast. I believe that is the most unique thing we are doing here at Penn State," Haque said.

Recently, the Materials Research Institute hired senior scientist Bernd Kabius, an expert at devising experiments for high-end electron microscopy, to help Penn State advance the microscopy field using the new Titan double aberration corrected TEM. Kabius and Haque have already begun what they hope will be a brilliant partnership.

"Bernd is a catalyzing agent for Penn State," Haque stated. "He and I are looking to do something revolutionary in the sense that we are designing ways to map temperatures inside the TEM. Right now I have some sensors that tell me what the temperature is at various points, but the technique we are going to develop is going to do temperature mapping in very high resolution at nanoscale."

Haque predicts that this will be like the difference between taking an image of a material with a conventional camera and the same image with an infrared camera. Whereas current TEM techniques show the structure and chemistry of materials, their proposed technique would provide a map of temperatures throughout the structure. They are also planning to make similar maps of electrical fields.

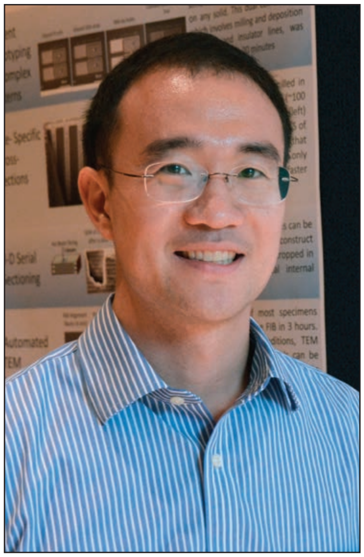
"Imagine you could map mechanical, electrical, and thermal fields right inside the TEM. Right now we have nothing. All we can do is see. But with fantastic TEM capabilities, if we add fantastic in situ capabilities, it will make sense of everything," Hague exclaimed.

A new thermal microscope could put Penn State on the map

Haque believes there is a big opportunity for Penn State in the field of micro and nanoscale thermal management, mostly because so few universities are well equipped with the instrumentation to do thermal work. One piece of equipment that is necessary is called a thermal reflectance microscope, a tool with the capability of measuring temperatures at very high resolution. With such an instrument, Haque suggested, he could immediately begin rounding up collaborators and training their groups to do their own measurements.

"When you have it (the TRM), everything goes fast. If we could get 10 collaborators, then definitely we could have something here at Penn State," he said. A few days ago, Haque was told by the College of Engineering that he was approved to purchase the TRM he had proposed and that it would be housed in the Materials Characterization Laboratory in the Millennium Science Complex. The instrument should be installed in 2016.

Aman Haque is a professor in the Department of Mechanical and Nuclear Engineering. He can be contacted at mah37@psu.edu.



As electronic devices become increasing common in our lives, they simultaneously shrink in size. Microelectronic devices whose dimensions are measured in micrometers (millionths of a meter) are common in military applications and likely to expand into other uses, such as communication and medical technologies. As is common with miniaturization, building devices at these dimensions introduces challenges that do not exist on larger scales.

SUKWON CHOI
MAPS HEAT IN MICROELECTRONICS

By Steve Miller

"New materials are being developed for their high power capability so we can build devices that are smaller and smaller," says Sukwon Choi, assistant professor of mechanical engineering. "As the power density increases, it gets hotter and hotter. As with all electronic devices, high temperature decreases reliability."

Measuring the operating temperature in small scale devices

The problem with using conventional temperature measurement techniques is that the devices have been shrunk below the limits of the thermometers and thermocouples that are used to measure heat on a larger scale. Thermocouple use is also restricted by the high voltage environment of the devices when they are in operation. Optical measurement techniques allow measurements in a noncontact, nondestructive way on the scale of current devices that typically measure about 5 µm in length.

Choi's group is developing techniques and instruments for thermal measurements at the micrometer scale in the Thermal Characterization Lab in Hammond Building on the University Park campus.

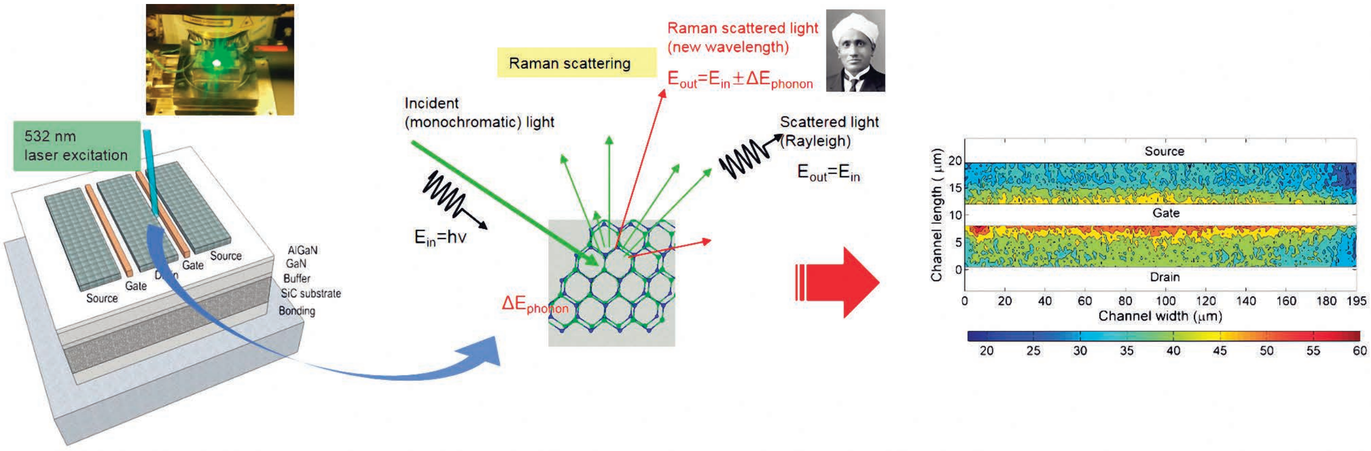
By incorporating four different thermal analysis techniques, they are able to look at multiple aspects of the thermal characteristics of microelectronic structures as they operate. According to Choi, his lab is the only facility in the United States that implements all four techniques in one place. Most university and government labs tend to focus on one of the four analytical methods.

Raman Thermometry

Chemical engineers have long used Raman spectroscopy, based on the change in energy of photons reflected from a surface, to determine the structure of crystalline materials. Because the change in energy is related to the lattice vibrations of atoms in the structure, changes in the vibration rate can be measured using Raman techniques. The relationship of vibration to temperature of a material allows the technique to be applied to temperature measurements of crystalline structures, such as semiconductors. The ability to focus the laser source of the incident photons gives this technique a high spatial resolution. Choi is able to resolve temperature readings at a length of about 1 micrometer or less. This allows him to profile the temperature characteristics across a transistor channel with dimensions of several micrometers.

Thermoreflective thermoimaging

While Raman optical methods are well suited to measurements in crystalline semiconductor materials, they are not applicable to metal. Choi applies a second technique to characterize the temperature



Raman thermometry measures the frequency of light reflected from a surface. The Raman effect, discovered by C. V Raman, causes some photons to be scattered with a different frequency than the incident photons. This change in frequency is related to the lattice energy of the surface, which can then be related to temperature.

of metals. Thermoreflective thermoimaging measures the reflectivity of a material as a function of its temperature. Because metallic surfaces are highly reflective, this analysis is particularly useful in devices that have a metal surface above the semiconductor. In addition, most semiconductor devices have metallic components, such as electrical interconnections. Combining these two optical techniques can increase the temperature profile information available for these devices, leading to a 2D image of the entire structure.

IR thermography

Infrared thermography is widely used by industry to measure temperature on larger scales. Among other applications, IR thermography measures heat loss from buildings, finds hot spots in industrial processes, and is even used to search for disaster survivors. Choi uses this analytical tool on a much smaller scale, but the principle is the same.

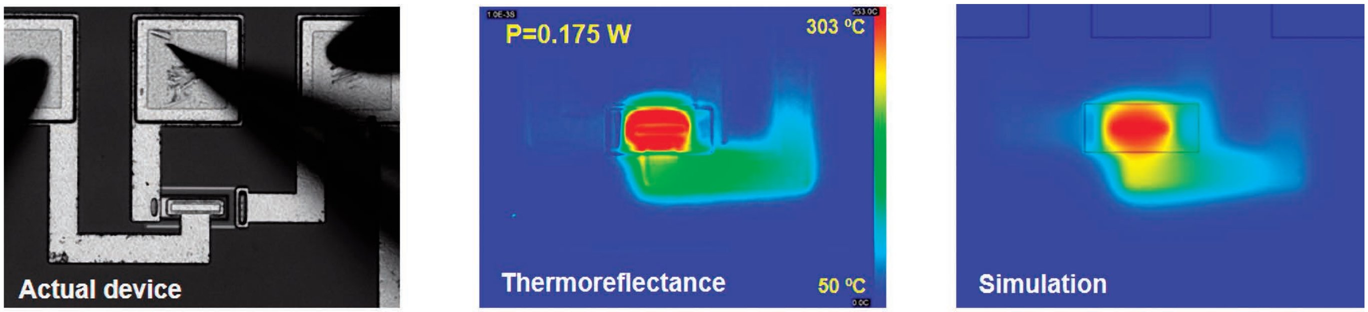
IR themography offers several advantages in microelectronic thermal characterization. While its resolution at about 3 microns is less precise than that of the Raman and thermoreflective techniques, it can be used to characterize the overall device temperature. Because infrared radiation is a characteristic of temperature, measurement is not dependent on the nature of the surface material. In some cases, it may measure the temperature of layers beneath the surface. For some applications, the decreased resolution is not critical for the analysis. On the scale of a microelectronic device, the measurement tends to give the average temperature of the entire device, not a profile across its surface. However, since the lifetime or reliability of such a device is frequently related not to the profile, but instead to the peak temperature during operation, IR thermography is an excellent method for failure analysis in microelectronics.

Photoluminescence

The final tool in Choi's lab is photoluminescence in which photons are absorbed by a surface, followed by release of a photon of a different wavelength. The instrument measures the difference between the energy absorbed and the energy emitted. It provides an additional tool for temperature measurement. The technique can also be used to measure the surface strength of a material.

Analytical Services

Choi works closely with several industrial partners to design and improve the instruments used in his lab. While the instruments may eventually be available commercially, the instruments themselves are very expensive and specialized. His current focus is on providing a service to users. By providing multiple techniques, he is able to reduce error in temperature measurements at the micrometer scale. He points



Thermoreflectance Thermal Imaging (TTI) measures temperature across a microelectronic device by correlating the reflectivity of a metal surface to the temperature of a metal. It can measure transient heating in nanosecond timescales to find the precise location and timing of heating events.

out that the users of many current methods operate using rules of thumb that were developed on larger scale applications and may not transfer directly to small scale analyses.

Bridging a Gap

Choi is interested in combining expertise in multiple disciplines to develop new engineering solutions. This approach comes from his work in optoelectonics at Sandia National Laboratory in New Mexico. "Because we pushed the limits so much and were developing new materials, we had some exotic configurations," he says. "We had to solve new problems in device design to make things work, and to do so we brought together experts from a wide range of specialties to work together."

Choi's goal is to train his students to think in ways that find solutions to the unique problems of microelectronics. As industries continue to develop new materials and push them to the limits of their capabilities, more and more complex problems will develop, he says. Choi plans to develop a hub to provide experts who are ready to tackle these problems related to new materials and higher power density.

"Right now we don't have those types of specialists," he says. "This will provide an opportunity to students to learn these techniques while also providing solutions to industry. There is a real need to solve microelectronics cooling issues through measurement."

While the role of a thermal engineer in physics has traditionally focused on heat transfer in solids and on computational fluid flow, this new focus couples thermal science with semiconductor science. Real devices have electric field profiles and heat generation profiles that depend on what voltage is applied, on the gain, and on the variables in materials. Choi wants his students to be able to calculate those heat generation profiles and electric fields and use that information to get a better understanding of what is going on inside the device, determine precisely how hot it is getting, and find the location of the heating.

"In industry labs, they don't have the people who are able to couple the two physics together," he says. "Sometimes they have two or three people who work together to figure out how to do that, but the language is different for people from different fields. I am trying to educate my students to understand the terminologies from electrical engineering and from material science and to come up with some basic simulations for coupling all these physics. I am bridging the gap."

Sukwon Choi received his Ph.D. in mechanical engineering from the Georgia Institute of Technology and was a post-doc at Sandia National Laboratories from 2013 to 2015. He came to Penn State in 2015.

Contact Dr. Choi at Sukwon.Choi@psu.edu

MATERIALS DAY 2015

A HIGH ENERGY LOOK AT THE FUTURE OF MATERIALS

WORKSHOPS, RECEPTION, AND KEYNOTE HIGHLIGHT DAY ONE

Day One of Materials Day 2015 kicked off with an industry Open House that attracted some 70, primarily Pennsylvania, companies. In the afternoon, workshops featuring faculty and technical staff walked participants through six different areas of expertise, from imaging of soft materials to modeling of the liquid/solid interface to thin film processing.

In the evening, Materials Day participants took a short walk across campus to the Business Building, with an imposing modernistic glass lobby, where an industry-graduate student reception and tabletop exhibit took place. During the event, students, faculty and industry guests streamed into the Business Building auditorium for the keynote address.

Dr. William Regli presented the keynote at Materials Day 2015, and people were buzzing about his presentation the rest of the week. Regli, Deputy Director of the Defense Sciences Office at DARPA, the Defense Advanced Research Projects Agency, gave an energized performance that hit on topics that will have big impacts on materials over the next decade.

As a computer scientist on leave from Drexel University, Regli was a perfect choice to propose a revolution in design in materials that will result from the merging of materials science and computation. “Our design tools don’t work for what we can make today. Are there new abstractions for modeling and some kind of human-machine symbiosis for design?” he asked.

To revolutionize design, we will need both big data and a means to share that data. He gave as an example the Sloan Digital Sky Survey, which changed the discussion in astronomy, by creating a detailed three-dimensional map of the Universe.

“We need a new form of computation that doesn’t separate data from computation,” he told the standing room only audience. And “Information and matter are interchangeable. How do we build bridges between them?”

DARPA would love to hear more of your ideas, he told the audience. “Great ideas are the ones that make you laugh,” he said, going on to explain that the best ideas have a fantastical quality that may at first hearing sound absurd.

DARPA, he reminded the crowd of scientists, founded the field of materials science and funded the original materials research labs. He asked his listeners to feel as though they are part of the DARPA family.

TECHNICAL TALKS AND INTERACTIVE POSTER SESSION FOCUS OF DAY TWO

Day Two of Materials Day began early with the opening talk delivered by MRI Director Clive Randall. Randall spoke of the link between MRI and industry, and stated that industry is deeply involved with educating our students for future industry needs. The link with over 400 industrial partners also helps faculty who are engaged write more compelling papers and grant proposals.

In light of this relationship, Randall introduced Dr. Phillip Yu, director of corporate science and technology at PPG Industries. PPG was just selected by Penn State as corporate sponsor of the year, and Yu spoke a few words in accepting the recognition. He said, “Penn State has supported PPG in four ways: by educating students, with state-of-the-art facilities, through the PPG Foundation in support of student research, and in student recruitment. Penn State has been an outstanding university, one that listens to industry.”

Randall also revealed the name of the three winners of the inaugural Humanitarian Materials Awards (see Inaugural Humanitarian Materials Awards Announced at Materials Day).

COMPUTATIONAL MODELING WILL CHANGE THE WAY WE STUDY MATERIALS

Adri van Duin gave the next technical talk, describing the importance of computational techniques in the future of materials design.

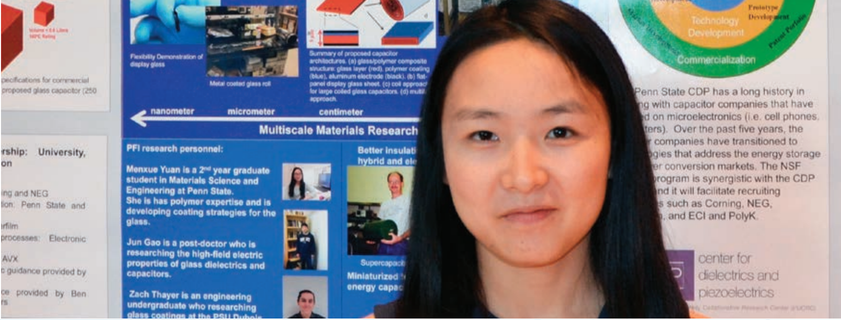
He compared the use of computation in materials choices to the way the pharmaceutical industry goes about drug development. Both are about saving time and money. Although materials are more complex, we have tools in hand to do like pharma does. But with materials design, the computational techniques have to cross the scales of size and time. At each interface of scale, Penn State has faculty able to make the transition. One such expert is the new head of the Department of Materials Science and Engineering, Susan Sinnott.

van Duin, who is professor of mechanical engineering and director of the Materials Computation Center, said that MCC and MRI are seed funding efforts to design methods to translate computational packages to industry. He described his recent work in which in some cases experiment led theory and his group helped experimentalists understand their results, and in other cases theory came first and helped experimentalists speed up their work tremendously.

The MCC will give experimental groups the ability to add a computational component to their research over a wide range of scales.

MULTIFUNCTIONAL COMPLEX OXIDES

Venkat Gopalan is the leader of an interdisciplinary research group (IRG) in the Center for Nanoscale Science (MRSEC) and a professor of materials science and engineering. He described complex oxides as being “essentially cages you can stuff a lot of the periodic table into.” In IRG1 his collaborators use knobs – chemical, strain, topology, geometry – to control the properties of layered ferroic materials.



One goal of their research is to electronically control magnetism, for instance in memory storage devices, which would be more energy efficient than current memory storage. "Can we get a material to have more than one property, such as both ferroelectricity and ferromagnetism?" Gopalan asked. Other potential materials, some being created at Penn State, include transparent metals and polar metals, and new dielectric materials, all based on complex oxides.

FABRICATION OF 2-DIMENSIONAL MATERIALS

The Center for Two-Dimensional and Layered Materials is a new center within MRI with 20-plus faculty and 45-plus students and post-docs. Joan Redwing, professor of materials science and engineering, chemical engineering, and electrical engineering is a center member with expertise in fabrication of 2D materials using chemical vapor deposition and atomic layer deposition techniques. These crystalline materials offer fascinating new properties when layered on top of each other. The properties depend on the types of materials and the number of layers. The field is new and largely unexplored, ripe for new advances in synthesis, she said.

With applications in optoelectronics, transistor electronics, and flexible electronics, the possibilities are endless. One new technique developed in her lab is a metal organic chemical vapor deposition/high pressure chemical vapor deposition process to fabricate bismuth selenide, a topological insulator that can be deposited on a plastic substrate at low temperature.

NANO-MOTORS BY 2025, A FANTASTIC VOYAGE

The pioneers of autonomous nano and microscale moving systems, Ayusmen Sen and colleagues at Penn State continue their work inspired by the 1966 film Fantastic Voyage, in which humans travel through blood vessels in a human body to try to destroy a life threatening blood clot. Although they are far from being able to clear blood clots or destroy brain tumors at the moment, they have still developed practical applications for their technology, including detecting and repairing cracks in bones and pumping oil stuck in dead-end pores in rock. Another group, not at Penn State, is using their ideas to pick up cancer cells in blood. Other applications under study are active drug delivery, enzyme pumps and sensors, attracting and eating nerve agents as a fuel, insulin pumps based on glucose levels in the blood, and sensors for toxic substances.

His colleague Tom Mallouk is using acoustic motors to drive nanorods toward cancer cells in a dish, where they are ingested by the cell and can then be manipulated to destroy the cell.

POLYMERS THAT WORK AT HIGH TEMPERATURE

Qing Wang's group in Materials Science and Engineering published a paper in Nature this year about their patented polymer nanocomposite material that combined polymer with boron nitride nanosheets to create a high-performing, high-temperature dielectric material for capacitors in power inverters in electric vehicles, aerospace applications, and electronics.

His material outperforms all current electroactive polymers, including those that require a cooling system. The material reduces current leakage and performs at 250 degrees C, where nothing else performs at all. It also has high thermal conductivity, light weight, is photo patternable, mechanically flexible and robust.

ADDITIVE MANUFACTURING OF METALS

Industries are beginning to invest in additive manufacturing, commonly known as 3D printing, because of reduced materials use, new design possibilities, and the possibility of creating custom components and one-off fabrication. But in metals, the thermal dynamics of laser fusion of the powder materials is not well understood. The complex thermal history of deposition will result in unique microstructures, said Allison Beese, an assistant professor in materials science and engineering.

Beese uses X-ray computed tomography to get 3D drawings of the internal structure of metal systems such as advanced titanium-aluminum alloys and stainless steel 304L. Her group is collaborating with theorist Zi-Kui Liu at Penn State and the Jet Propulsion Laboratory on functionally graded materials that have gradual variations in structure and composition.

THE FUTURE OF POLYMERS PROCESSING

New and advanced materials systems are forcing a change in the processing of polymer/plastic materials, according to Greg Dillon, who is associate director of technology transfer at Penn State Behrend. Located in Erie, PA, the Behrend campus is home to a high tech hub for polymer manufacturing research and testing. They use industry provided injection molding equipment that is exactly the same as that used on a production line. Ten percent of plastics produced in the U.S. touch Erie, he said.

Processing is becoming far more efficient and saving a few seconds in a process can end up saving billions of dollars, considering the huge scale of production. New developments in polymer processing include conformal cooling by designing a mold built with additive manufacturing so cooling can be controlled with channels in the mold, micromolding for small parts such as lab-on-a-chip, microcellular foaming gas assist technology in which gas is pumped through the plastic melt, and co-injection molding that combines materials.

The future, he said, is getting the materials scientist involved in the process, especially for fast-growing areas such as medical implant materials.

STUDENTS/FACULTY PRESENT THEIR LATEST RESEARCH

In the Day Two poster session, over 120 posters detailed the latest research results of the faculty groups working in the materials community at Penn State. From the fundamental to the applied, the research covered biomaterials, electronic/photonic materials and devices, coatings and nanomaterials, materials characterization and materials processing and manufacturing. Students met potential employers and practiced presenting their findings in a polished fashion. The overall result was one of the most enjoyable and successful Materials Day in memory.

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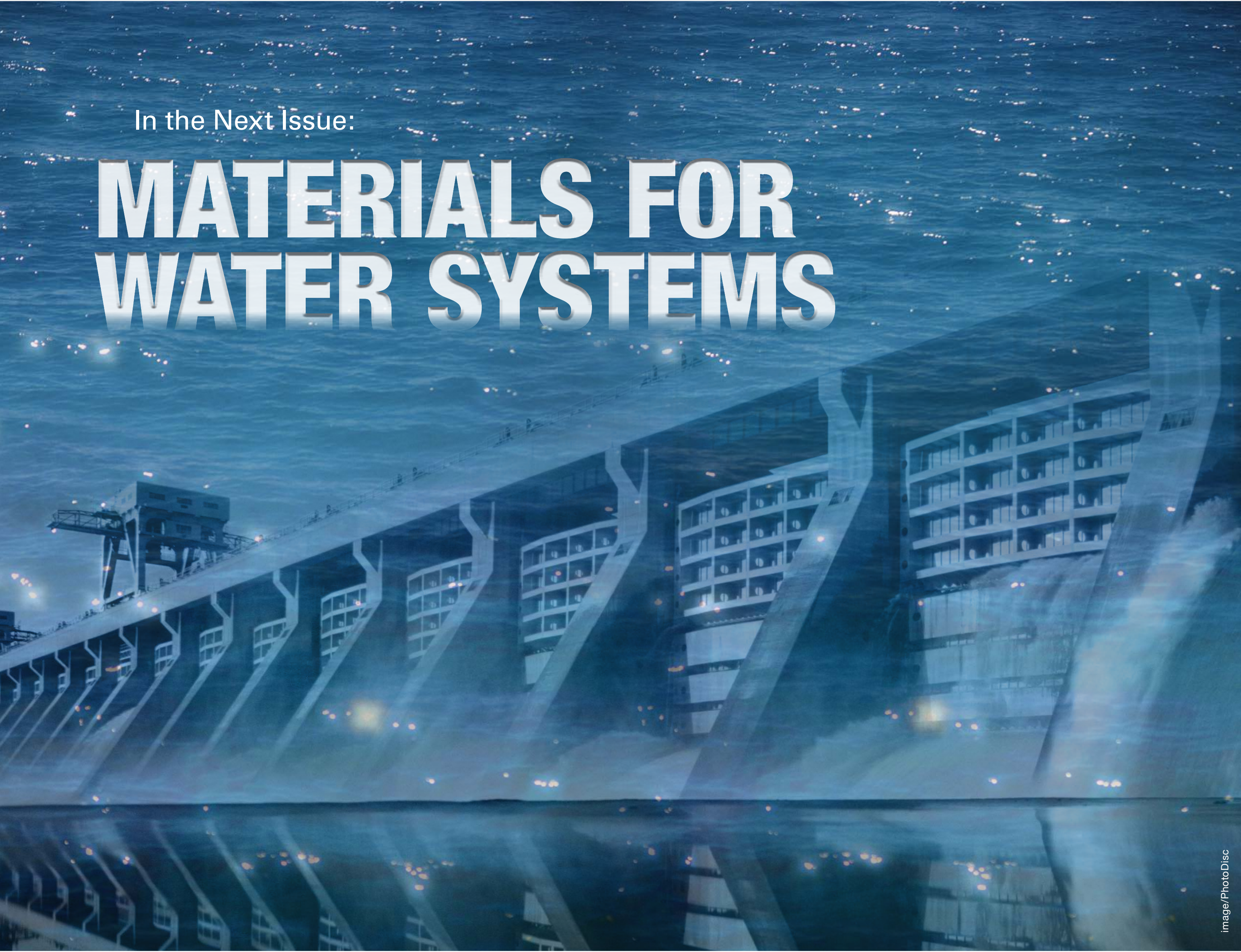

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