

### Applications, Transistions and Innovations



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"What would happen if we could arrange the atoms one by one the way we want them...?" - Richard Feynman Nobel Prize in Physics, 1965

"What's new is the notion that we can actually build new nano-objects that have never existed before that increase our arsenal of capabilities."

- Richard Smalley Nobel Prize in Chemistry, 1996

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#### Introduction

In a speech at the California Institute of Technology on December 29, 1959, Richard Feynman invited scientists to enter a new field of physics enabled by the atom-by-atom manipulation of matter. His talk, *"There's Plenty of Room at the Bottom"*, inspired the new field of nanoscience and technology, from which he envisioned an enormous number of practical applications in computing, information technology, biology, and mechanical systems. Almost fifty years after Feynman's talk, nanotechnology is now responsible for many new products and capabilities, not only in the areas discussed by Feynman, but also in health care, communications electronics, textiles, automotive and recreational industries.

While a great deal of practical benefit has already been achieved from nanotechnology applications, there are many more opportunities in areas not even imagined earlier. Significant worldwide efforts are motivated by these opportunities, and are viewed to be essential to national prosperity and defense. The United States has long been a nanotechnology leader, with strong activities in the commercial, industrial, energy and defense sectors. The Air Force Research Laboratory (AFRL) is the world's pre-eminent laboratory for air, space and cyber technologies, and has a strong history of discovery and leadership in nanotechnology. Focused on satisfying important Air Force needs, nanotechnology innovations from AFRL have resulted in important transitions and warfighting capabilities.

The purpose of this booklet is to introduce the AFRL nanoscience and nanotechnology enterprise by outlining the broad areas of strategic investment and briefly describing the way that AFRL defines, integrates and conducts its expansive nanoscience and technology effort. Specific successes are given where results from these efforts have made an important difference for the Air Force, and where they may do so in the future. Twenty-four nanoscience and technology successes are selected that include warfighting capabilities currently used in the field, technology transitions being validated in systems-level testing, and scientific discoveries that may help change the way the Air Force defends America in the future.

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#### What is Nanoscience and Nanotechnology?

*Nanoscience* is the study of materials at length scales smaller than those where conventional physics apply (less than about one micrometer, which is equal to one thousandth of a millimeter or one thousand nanometers and is roughly 1/100<sup>th</sup> the diameter or a human hair), and larger than those where atomic physics dominate (more than a few tenths of a nanometer). It combines contributions from many scientific disciplines, including biology, chemistry, physics, optics, engineering, computer sciences, and mathematics. *Nanotechnology* is the application of nanoscience by the practical formation of nanoscale structures and integrating them into materials, devices and products. There is no single length scale that defines nanoscience and nanotechnology, but it typically ranges from several tenths of a nanometer to several hundred nanometers.

Why are the properties of materials so different at these length scales? The reasons can be as simple as the fact that more and more atoms are close to defects like a surface or internal interface as the size approaches nanometer dimensions. These defects have properties that are very different from the bulk, and a high surface-to-volume ratio is responsible for many useful effects, including highly reactive munitions and fuels and ultra-sensitive chemical and biological sensors. On the other hand, the reasons for the unique properties of nanomaterials can be as complicated as the quantum confinement of electrons into different energy states that give new solid state lasers and infrared detectors.

These length scales apply to the size of nano-particles that can be discrete or embedded in conventional materials. They can also apply to the thickness of individual or multiple layers in engineered laminates. The size and spacing of pores and internal interfaces give new properties when arrayed at nanometer length scales. And engineered materials and devices have been produced from amazing combinations of pillars, platelets, tubes, rods and molecules with nanometer dimensions. These features can interact with light and other electromagnetic energy; they can interact with magnetic domains for improved superconductivity; they strengthen metals by resisting the motion of dislocations responsible for deformation; they force electrons into unique energy states; and they give exceptionally high surface areas for a wide range of applications.

#### Nanotechnology at the Air Force Research Laboratory

AFRL scientists and engineers have a rich tradition of excellence in aerospace research and development at nanometer length scales to establish compelling new Air Force capabilities. The AFRL nanoscience and technology enterprise is led by a talented group of scientists and engineers within the AFRL Directorates that conduct research and that define, initiate and lead contractual programs with academia, industry and the other Services. It also includes significant international investment and collaboration. The AFRL nanoscience and technology activity is intensively multi-disciplinary and, like AFRL itself, is geographically diverse and is distributed at Air Force bases and facilities across the United States. This multi-disciplinary and geographically diverse activity is integrated across Directorates and coordinated with the other Services through the AFRL Nanoscience and Technology Strategic Technology Team (see the following section).

Major strategic themes include *nanomaterials* for adaptive structures, responsive coatings, thermal control and system protection; *nanoenergetics* for munitions, fuels and high energy density generation and storage; *nano-devices* for sensors, millimeter and microwave receivers and emitters and signal processors; and establishing the *scientific foundations* for biological interactions with nanostructures (see the section on health and safety), the assembly of nanostructures and the theory, modeling and simulation of nanomaterials and devices. AFRL is the leader in nanoscience and technology for military applications of directed energy weapons, optical materials, infrared photodetectors and high-yield energetic materials for fuels and munitions.

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#### The Air Force Research Laboratory Nanoscience and Nanotechnology Strategic Technology Team

AFRL established Strategic Technology Teams (STTs) to focus and integrate selected high impact technologies that span several Directorates and have enduring strategic value. As the first AFRL STT, the NanoScience and Technology (NST) STT develops, advocates and conducts an integrated strategic plan. The NST STT community of scientists and engineers anticipates and determines the most compelling Air Force needs through dialog with technology integrators users and by evaluating recent warfighting assessments such as Focused Long Term Challenges (FLTCs) and Air Force Vision 2020. These needs are paired with emerging nanoscience and technology advances to identify opportunities for the AFRL nanoscience and technology strategic plan. Evaluation criteria for candidate strategic technologies include a compelling warfighter need; a pervasive technology impact; unique Air Force requirements with no commercial drivers; and established Air Force leadership. Proposed programs addressing the highest priorities are developed by the NST, reviewed by the AFRL STT Leadership Council and, if approved, are developed into executable programs.

In addition to developing a strategic plan and executable programs, the AFRL NST STT fosters collaboration within AFRL, with academia and industry, with other Services and with the international community to leverage strengths and to best utilize available resources. It serves as a single point of contact within the Air Force, the Department of Defense and the nation for internal and external information requests. And it provides an objective voice within the Air Force to assess nanoscience and technology opportunities to the warfighter. Since its inception, the AFRL NST STT has successfully established and executed an integrated strategic plan by fostering a culture that encourages and rewards integrated planning and collaboration.

#### Introduction to Air Force Research Laboratory Nanoscience and Nanotechnology Successes

Important nanoscience and technology advancements in the AFRL Directorates have produced many compelling Air Force transitions and operational capabilities. The following pages give 24 selected nanoscience and technology advances from AFRL. These successes are organized by maturity, and include 6 fielded applications that are already in use; 8 technology transitions being validated, scaled up and certified in system-level testing; and 10 innovations that may enable future paradigm shifts. These successes come from the strategic emphasis areas defined by the AFRL nanoscience and technology Strategic Technology Team and address important Air Force themes such as access to space and protection against asymmetric threats. These advances come from across the Directorates in AFRL. The Air Force Office of Scientific Research (AFOSR) plays a vital role in incubating many of these successes, which are developed and transitioned through the remaining Directorates.



#### Nano-Layer Midwave Infrared Detectors and Cameras

**Accomplishment:** This research produced the world's first successful 'staring' (continuous imaging) infrared sensors by developing a 2 nanometer thick platinum silicide (PtSi) layer on a silicon substrate. The basic research to establish the process of internal photoemission responsible for the infrared signal was developed and transitioned into production of an infrared camera technology that dominated the field for more than a decade.

**Impact:** AFRL PtSi research revolutionized the field of infrared imaging and target detection. Field testing established the midwave infrared band as the international industry standard for long-range imaging through the atmosphere. PtSi infrared cameras dominated the field for almost 15 years since the early 1990s, when they were used in U-2 aircraft during the Gulf War. These cameras were installed in the entire B-52 fleet in the 1990s, giving a 50-fold increase in reliability and a 3-fold increase in the warning and detection range relative to preceding infrared cameras. The increased reliability saved the AF \$12 million per year by reducing maintenance costs in the B-52 fleet. As a result of this accomplishment, the leader of the PtSi effort was elected to the National Academy of Engineering and was awarded numerous engineering and professional society awards.



**Motivation and Approach:** Previous infrared sensors gave images by scanning a single pixel or a line of pixels over the area of interest. As a result, the detector spent little time on specific points of interest and the final image had to be reconstructed. By contrast, staring sensors allow the entire image to be collected at once, similar to taking a conventional photograph. The use of commercial silicon technology and the low electronic noise of the photoemission process increased the signal to noise ratio in the image. This greatly improved the reliability of information in the image, and opened up new image processing techniques that remain in use today.

To achieve this capability, thin PtSi films were created on silicon to absorb infrared radiation with a wavelength from 3-5 µm, producing an electronic signal at the PtSi/silicon interface by internal photoemission. The maximum efficiency of these devices occurs when the PtSi layer is only 2 nm thick. The AFRL team discovered and leveraged this behavior to create infrared cameras, and they also invented infrared image processing and calibration methods that maximized the camera's detection capabilities. Many of these techniques were adopted throughout the international infrared community, and are now used for detection in all wavelength bands and by a variety of sensors. Fabrication was transferred to commercial production at US silicon wafer manufacturers. PtSi/silicon cameras were installed in the U-2 during the Gulf War, where they were used to locate and identify placement of land mines and other targets of military interest. PtSi/ silicon cameras were installed in the entire B-52 fleet in the 1990s - the prototype was built in-house by the AFRL research team.

**Team:** The research team at the Sensors Directorate and its predecessor organizations was led by Dr. Freeman Shepherd, with major contributors from Charlene Caefer, Steven DiSalvo, Dr. William Ewing, Darin Leahy, Charlotte Ludington, Dr. Jonathan Mooney, James Murrin, Paul Pellegrini, Dr. Jerry Silverman, Virgil Vickers, Melanie Weeks, and Dr. Andrew Yang. The basic research was funded by the Air Force Office of Scientific Research and the development and industrial transition was funded by the Sensors Directorate.

Applications

# Nano-Particles Enable Superconducting Wire for

**Compact Power Systems** 

**Accomplishment:** Nano-particle additions have increased by more than 10 times the electrical current carrying capability of high temperature superconducting (HTS) wire. This breakthrough increases efficiency and operating temperature and enables a dramatic 2-4 times reduction in power systems size over conventional generators.



Impact: HTS-coated conductor enables compact sources of high-power electricity that are essential to national defense. Military uses include power generators, gyrotron magnets, power converters, transformers, motors, primary power cabling, and magneto-hydrodynamic magnets. HTS conductors reduce the size of the power generator and the microwave-producing gyrotron magnet for airborne and ground-based active denial systems that will provide non-lethal anti-personnel capabilities via high power microwaves. This technology reduces power generator cooling loads and refrigeration system size by over 80 times. First demonstrated at AFRL, this advancement has become the industry standard for commercial HTS materials and has launched a new field of study and development.

**Motivation and Approach:** Since their discovery in 1986, HTS materials have been pursued for compact power systems. Previous state-of-the-art HTS conductors enabled generators that could produce several megawatts of electrical power while using only about 40% of the mass and volume of conventional generators. However, the high magnetic field within the conductor limited electrical supercurrents near the 77K operating temperature, reducing the power produced and

increasing cooling requirements. These debits added significantly to power system size and cost, reducing the benefit of earlier HTS technology.

AFRL scientists demonstrated that HTS currentcarrying capability is dramatically improved by adding a high density of insulating nano-particles. These nano-particles pin the moving magnetic flux, allowing larger supercurrents and higher electrical current-carrying capacity. Pulsed laser deposition was used to create a multilayered superconductor with a carefully controlled nano-particle dispersion, essential for achieving this effect. This major advancement allows development of power sources only one fourth the size and weight of conventional units. This technology has been commercialized in the international superconducing industry, and has enabled continued progress toward the development of compact power sources critical for Defense applications such as that used by the Airborne Active Denial Technology.



**Team:** Dr. Paul Barnes and Dr. Timothy Haugan of the Propulsion Directorate were responsible for the technical innovation leading to this accomplishment. Scale-up and commercialization were achieved at SuperPower, Inc. and American Superconductor Corp. through a Defense Production Act Title III program and dual use funding from the Propulsion Directorate.

#### Nickel Nano-Strands for Aircraft Lightning Strike Protection and Electro-Magnetic Shielding

**Accomplishment:** Electrically conductive structural composites, polymers, paints, adhesives and ceramics have been produced by adding nickel nanostrands that are 100-150 nanometers in diameter and up to a millimeter in length. Manufacturing processes have been established to apply these new materials to a range of military applications.

**Impact:** Significant protection from lightning strike damage, required for all-weather aircraft operation, has been demonstrated in component-level testing of composite structures with nickel nanostrands. Conductive polymers using nickel nanostrands are being validated for shielding of electronic components from electromagnetic pulses, saving 150 lbs per aircraft over the current metal shielding. Electrically conductive coatings using nickel nanostrands are now fielded in other critical DoD applications.



Motivation and Approach: Commercial aircraft are struck by lighting 1-2 times a year, and all-weather operation required for military aircraft increases the chance of a lightning strike. Graphite/ epoxy composites are widely used in aircraft skins and structures but do not have good electrical conductivity due to the composite ply architecture and low breakdown current (the current at which a material no longer conducts electricity) of graphite fibers. The high current (200,000 amps) and voltage (750,000 volts) of a major lightning strike vaporizes the epoxy resin and destroys the graphite fibers, producing significant structural damage. The electromagnetic pulse can also damage critical electronic components in the aircraft. Structural composites are presently protected by adding metal meshes or foils that add significant cost and weight, are damaged by corrosion, and are difficult to repair. Electronics are shielded with metal boxes that add up to 150 lbs per aircraft.

Polymers, including epoxy, are usually nonconductive, but adding only a small volume fraction of nickel nanostrands provides a conductive path due to the nanometer-sized diameter and the millimeter-sized length. Addition of only 2% by volume of nickel nanostrands doubles the electrical conductivity of a graphite/epoxy structural composite. In this accomplishment, nickel nanostrands were developed at Metal Matrix Composites Company, LLC and were characterized and incorporated into conventional structural composite processing and manufacturing at the Materials and Manufacturing Directorate. Techniques were established to produce conductive polymeric surface films by integrating nickel nanostrands into spray painting, wet coating and brushed gel coatings. Nickel nanostrands have also been added to adhesives, thermoplastics and ceramics. A wide range of applications have been identified and are under development and certification testing or have already been inserted into fielded applications.

**Team:** Research at the Materials and Manufacturing Directorate is led by Max Alexander, with significant contributions from Dr. Jennifer Chase Fielding, Heather Dowdy and Brandon Black. Manufacturing and engineering contributions were funded by an Air Force Small Business Innovation Research (SBIR) program with the Metal Matrix Composites Company, LLC and Eclipse Composite Engineering.



**Applications** 

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#### Nano-Coating Enables New Class of High-Power Microwave Devices

**Accomplishment:** High power microwave devices with enabling improvements in power output, size, weight and lifetime were developed, produced and tested. These benefits were achieved with a new cathode that relies on a cesium iodide coating roughly 100 nanometers thick.



**Impact:** This advancement is currently used in all Air Force high-power microwave sources. It has enabled counter electronic warfare and plays a vital role in Airborne Electronic Attack by reducing system size, weight and power consumption. The detonation of improvised explosive devices (IEDs) at a distance was demonstrated in field tests and is now possible. This cathode material was transitioned to the commercial sector to generate non-weaponizable X-rays for scientific research, non-destructive evaluation and medical imaging.

**Motivation and Approach:** High-power microwave devices emit short bursts of very high energy microwave radiation that can be focused into a beam. These are weaponizable devices that can be used in counter-electronic warfare to defeat adversary computers, communication networks and missile navigation and control at a distance. High-power microwaves can also be used to detonate improvised explosive devices (IEDs) at a distance. The effectiveness of earlier high-power microwave devices was severely limited by field emitter cathodes that suffered from short lifetimes, or thermionic emitter cathodes that had low power conversion efficiency and high weight. Significant improvements in cathode technology were needed to make high-power microwave devices practical.

This accomplishment developed and tested highpower microwave devices with a new cathode material consisting of a 'carpet' of carbon fibers with a cesium iodide coating that is roughly 100 nanometers thick. The cesium iodide coating reduces the energy needed to extract electrons, which are then passed through a magnetic field to produce microwaves, from the carbon fiber. This lower work function gives a five-fold increase in power conversion efficiency, from less than 10% to over 40%, significantly increasing the microwave beam power and reducing the size and weight of the device. The cesium iodide coating also reduces cathode damage, dramatically extending device lifetime from less than a few thousand pulses for earlier cathodes to over 1 million pulses. Cesium iodide coatings much less than 100 nanometers did not significantly reduce the work function, and thicker layers inhibited electron emission dramatically.



**Team:** The research team included Dr. Don Shiffler, Dr. Michael Haworth, Dr. Ryan Umstattd (now at Oak Ridge National Laboratory), Dr. John Luginsland (now at NUMEREX, Inc.) and Dr. Susan Heidger at the Directed Energy Directorate. Additional significant contributions were made by interactions with Energy Sciences Laboratory Inc., SAIC Inc., Sandia National Laboratory and Ktech Corp.

#### Commercialization of Nano-Composites for Space Systems Insulation

**Accomplishment:** Nanostructured silicate molecules, polyhedral oligomeric silsesquioxanes (POSS), were developed and commercialized. These POSS molecules have been dispersed in conventional polymers, producing nano-composite materials with improved thermal and physical properties.



**Impact:** POSS has been added to solid rocket motor insulation, achieving a major goal of 25% reduction in the insulation erosion rate. This results in a 22% decrease in insulation weight and a 4% increase in booster payload capabilities for launch systems such as the Atlas V solid rocket motor. POSS addition to Kapton plastic, used for thermal protection in satellites, delivers an increase in service life of 5 years or more. Commercialization has reduced the minimum price of POSS from \$1000 to \$20 per pound.





Motivation Approach: and Organic materials such as plastics and rubbers are attractive aerospace insulation materials due to their low weight, low thermal conductivity and processibility. However, they have poor resistance to aggressive space systems environments that include high temperatures and corrosive gases in launch systems and erosive atomic oxygen in the orbit of most satellites. The silicate structure of the POSS core gives good stability in aggressive environments, and the chemical groups attached to the corners of the silicate molecule core allow POSS to be easily incorporated into a wide range of organic materials. POSS was first added to organic materials at AFRL. This accomplishment has led to significant improvements in a broad range of material properties. The processability of resulting nano-composite materials is retained as a result of the nanometer-sized POSS additions, so that existing manufacturing processes can be used. Commercialization has been achieved through a Cooperative Research and Development Agreement (CRDA) and patent licensing agreements with Hybrid Plastics, Inc.

**Team:** This advancement was accomplished in the Propulsion Directorate by a team of 11 scientists and engineers, led by Dr. Joe Mabry. A spin-off company, Hybrid Plastics, Inc., was created in order to commercialize this new technology.

#### Dualband Quantum Well Infrared Camera for Target Identification

**Accomplishment:** The first dualband infrared detector array operating in the longwave / longwave regime was developed and characterized. This detector was made possible by a unique quantum well infrared detector architecture.

**Impact:** This advancement provided the technical basis for follow-on development of a midwave / longwave dualband detector array and camera with improved sensitivity needed for remote temperature measurement and target identification. This camera has been validated in field tests to identify and track airborne vehicles and to give early missile warning and identification. These cameras can be used for a wide range of other applications, including buried landmine detection and astronomical observations.

Motivation and Approach: Infrared cameras are used for imaging of land-based threats such as tanks, missile launchers and buried landmines; for early missile warning and tracking; and for space situational awareness. Until recently, conventional infrared detectors based on mercury-cadmiumtelluride or indium-antimony typically could detect only one specific wavelength of infrared light, but at least two wavelengths are needed simultaneously to measure temperature. The ability to quantify temperature, rather than simply to detect heat, gives the added essential capability to positively identify targets. Mercury-cadmium telluride can now provide dualband detection, but with relatively low signal uniformity, only limited detector array size and relatively high noise that depends on the signal frequency. Dualband detection can also be achieved with two different cameras, or one camera with a complex set of filters that are inserted into the light path, but these approaches add considerable cost, weight, volume and maintenance.

Quantum well infrared photodetectors consist of 30 to 50 pairs of alternating semiconductor layers such as gallium arsenide and aluminum-doped gallium arsenide. Each layer is 5-10 nanometers thick, which forces electrons into specific energy levels that absorb infrared radiation at a specific wavelength that can be tailored by controlling the composition and thickness of the layers. Dualband detectors are constructed by placing a set of layers tuned for one wavelength on top of another set of layers tuned for a different wavelength. Each stack absorbs infrared radiation within a specified wavelength band, but allows other wavelengths to pass through. This design approach was developed and validated in this accomplishment. The detectors were developed at the Jet Propulsion Laboratory through funding from the Air Force Office of Scientific Research and the Space Vehicles Directorate, they were characterized for the space environment with a low thermal background at the Space Vehicles Directorate, and they were transitioned into commercial applications by the Jet Propulsion Laboratory and Indigo Systems, Inc. (now part of FLIR Systems, Inc.) through funding from the Missile Defense Agency.



**Team:** Research at the Jet Propulsion Laboratory was led by Dr. Sarath Gunapala. Research at the Space Vehicles Directorate was conducted by Dr. Dave Cardimona and Dr. Anjali Singh (currently with Northrop Grumman), and this technology has been transitioned by Indigo Systems, Inc. (now part of FLIR Systems, Inc.).

#### Semiconductor Quantum Well Lasers for Aircraft Self Protection



**Accomplishment:** Semiconductor quantum well lasers have been developed to protect aircraft from shoulder-launched heat-seeking surface-to-air missiles. Prototype systems have been manufactured and systems-level performance is being validated in field testing.

**Impact:** Semiconductor quantum well lasers offer continuous operation and tunability over a wide range of wavelengths used by heat-seeking systems, giving significantly improved protection against current and next-generation air-to-air and ground-to-air threats. These high-efficiency lasers reduce complexity of the protection system, increasing the mean-time between failures by thousands of hours and reducing cost by \$600,000 per shipset.

Motivation and Approach: Air-to-air and ground-to-air heat-seeking missiles pose an important threat to Air Force assets. Low altitude flights required for combat support make transport aircraft and helicopters especially vulnerable to attack by shoulder-launched heat-seeking missiles. Current countermeasures protect Air Force aircraft by sending pulses of infrared energy to 'jam' the infrared sensor in the missile that is tracking a targeted aircraft. However, current countermeasures do not protect against sensors in the far infrared regime, have a short mean time between failures, and are expensive. Further, next-generation heatseeking missiles will use more advanced 'staring' infrared sensors that continuously monitor the infrared signal of the tracked aircraft, and so cannot be jammed by a pulsed signal.

The solid-state lasers developed here use quantum wells that consist of semiconductor materials deposited in layers from 0.3 to 3.0 nanometers thick. These quantum wells concentrate electrons into discrete energy bands, producing laser light with wavelengths that cover a broad range in the infrared spectrum. Layer thickness and composition are controlled to produce lasers operating at the designed wavelength, power, and beam quality. Infrared countermeasure systems using this technology give protection across the full range of threats, including the far infrared regime and 'staring' infrared seeking sensors. Test and evaluation activities are underway at the Sensors Directorate and at the Navy. Several prototype systems have been produced and are now undergoing field tests.



**Team:** These advancements were led by Dr. Andrew Ongstad and Dr. Ron Kaspi at the Directed Energy Directorate and Mark Wunderlich at the Sensors Directorate. The Advanced Technology Demonstration program was run by Lt. Rachel Englund. Prototype systems are produced by Aculight Corp.

### Nano-Taggants for Biological Threat Detection

**Accomplishment:** A nano-taggant system has been developed that can be placed on living insects. The labeling, release, recapture and identification of tagged insects was demonstrated for the first time.

**Impact:** Nano-tagged insects can gather illicit chemical, biological or radiological materials from the environment they travel through and deliver them for analysis, giving both composition and origin of these threats. This accomplishment provides the first demonstration of the most challenging part of the nano-taggant detection process that includes insects capture, tagging, release, recapture and positive identification.



**Motivation and Approach:** Military operations require early detection and analysis of chemical, biological and radiological materials used against deployed forces and civilian populations. Current sensing approaches rely on stationary collectors that require physical visits, sometimes several times a day, to monitor the collectors and verify positive indications. These fixed sensors require placement and monitoring in areas controlled by friendly forces and are subject to tampering in urban environments. Insects marked with nanotaggant technology offer an exceptionally low profile approach to gather environmental data over a much wider range of areas without alerting the target.

The process starts when nano-taggants, composed of metallic nano-particles bound to fluorescent semiconductor quantum dots, are sprayed on the wings of captured insects. The metallic nanoparticles have specific alloy concentrations, which allow the labeled insects to be identified after recapture. The insects are released into the area to be monitored for a chosen period of time, and are later recaptured. The recaptured insects are exposed to ultraviolet or visible light that makes the nano-taggant quantum dots glow, allowing the tagged insects to be identified with hand-portable detectors that are commercially available and usable by field-grade personnel. The composition of the metallic nano-particles attached to the quantum dots is then read like a barcode using laser-induced breakdown spectroscopy, indicating the specific lot of insects and linking them with the environment that they sampled. Any substances acquired in the insects' travels are also extracted and analyzed. The origins of the new materials are inferred from knowledge of where the insects were released and subsequently recaptured, in much the same way that the movements of tagged birds, fish or sea turtles are now routinely traced. In this demonstration, about 5% of the recaptured flies were previously labeled and released, showing for the first time that insects can be released and recaptured in this fashion.



**Team:** Scientists from the Human Effectiveness Directorate, led by Dr. Jonathan Kiel, modeled the natural behavior of target insects and developed nanoscale labeling materials in cooperation with NovaCentrix (supplier of metallic nano-particles) and Evident Technologies (supplier of quantum dots). USDA entomologists collaborated in the field tests and collection of insects. The Army Research Laboratory developed the analytical method for identifying the specific nano-taggant.

#### Self-Protection and Self-Healing of Polymer Nano-Composites

**Accomplishment:** Self-protecting and selfhealing polymer nano-composites were conceived, produced and tested. Up to an order of magnitude improvement in durability was established in simulated launch and orbital space environments.



**Impact:** This accomplishment demonstrates a fundamentally new class of self-protecting and self-healing organic polymers that has a strong potential to improve access to space. An order of magnitude improvement in the durability of solid rocket motor insulation can reduce launch weight and increase the volume available for propellant, significantly increasing range and payload. Improved processiblity can eliminate the leading source of failure in current solid rockets. An order of magnitude increase in durability of organic polymers in orbital environments can decrease satellite weight and significantly increase mission lifetime and reliability.

**Motivation and Approach:** Organic polymers are essential materials due to their useful properties, light weight and exceptional processibility, but they are seriously damaged by aggressive space environments. Very high temperature gases burn organic polymer insulation used to protect solid rocket motor cases to a non-protective char. Up to 50% by volume of fillers are added to reduce the erosion rate, adding significant cost and weight, reducing the volume available for propellant, and requiring complex hand-processing that produces bondlines that are the leading cause of rocket motor failures. Satellites are exposed to strong ultraviolet radiation, atomic oxygen, and sub-atomic particles that rapidly degrade and remove organic polymers. Protection is currently achieved with ceramic coatings, by blending with inorganic polymers and micron-scale fillers, or copolymerization. Coatings provide only nominal protection in space, where coating damage cannot be detected or repaired. The other approaches decrease the polymer properties. All of these approaches add weight and considerable cost.

Polymer nano-composites of consisting nanometer-thick silicate or alumino-silicate clay platelets dispersed in an organic polymer matrix were conceived and produced at AFRL. Testing in simulated launch and orbital environments preferentially removed the organic polymer, leaving the clay platelets that form a protective ceramiclike surface layer. In ablation tests, the layered clay nano-particles melt to form a self-healing, high viscosity liquid that reduces damage by filling holes. Less than 1% by volume of layered nanoparticles gives protection equivalent to state-ofthe-art organic polymers with 15-30% by volume of filler, and an order of magnitude reduction in damage rate was achieved with 8% by volume of clay nano-platelets. The lower volume fraction of this approach reduces weight, increases reliability via processing that eliminates bondlines, and drastically reduces cost. Since protective layer formation is an inherent property of the bulk polymer nano-composite, these materials are self-protective and self-healing, providing a fundamentally new concept and capability for durable space materials.

**Team:** This research was conducted at the Materials and Manufacturing Directorate by Dr. Rich Vaia, Dr. Maj. Derek Lincoln, Shane Juhl, Dr. Hao Fong (now at the South Dakota School of Mines and Technology) and Dr. Jeff Sanders, and at the Propulsion Directorate by Dr. Shawn Phillips and Dr. Joe Lichtenhan (now at Hybrid Plastics).



#### Nano-Membrane Flexible Electronics for Surveillance Radar

**Accomplishment:** New processing techniques for the formation, doping and transfer of silicon nanomembranes were developed and used to produce the world's fastest flexible electronic devices.

**Impact:** Created specifically for Air Force missions, these high speed flexible electronics enable largearea, conformal radio-frequency surveillance radar in manned and unmanned aircraft and in spacecraft. The large active area improves the radar signal, and conformal attachment reduces aerodynamic weight (by 90%), drag, complexity and cost (by 90%) associated with current protruding radar antennae. Application to conformal radio-frequency antennae is now being evaluated by a major US aerospace manufacturer for next-generation military aircraft.



**Motivation and Approach:** Thin electronic circuits on flexible polymer substrates offer dramatic advancements in airborne (manned or unmanned) and spaceborne surveillance radars essential to the Air Force and to national security. Their primary

advantage over conventional rigid-chip systems is their thinness and flexibility, which allow conformal attachment to irregular surfaces, mounting into limited space, and resistance to damage from impact and vibration. Conformal attachment dramatically reduces the complexity, weight and drag compared to current protruding radar antennae, thus significantly improving the operational reliability of the transport aircraft. Flexible electronics are also important in missiles where space for electronics is very limited but high processing speed is needed. The electronics developed here are very robust against damage from impact and severe vibration, making them valuable for rockets and smart bombs, where significant vibration is unavoidable.

The critical component in flexible electronics is a very thin layer of silicon that is doped (alloyed with very small amounts of other elements) to give a high charge carrier mobility. Silicon is typically rigid, but is flexible when produced as 200 nanometer-thick films and bonded to a polymer substrate. However, previous processing methods were not able to perform the high temperature doping process without damaging the flexible polymer substrate. In this work, the high-temperature doping was performed while the silicon nano-membrane was supported by a silicon substrate, after which the doped silicon nano-membrane was transferred at low temperature to a flexible polymer substrate.

**Team:** This accomplishment was achieved by Prof. Zhenqiang Ma and Prof. Max Lagally at the University of Wisconsin-Madison. Funds were provided by the Air Force Nanotechnology Initiative Program at the Air Force Office of Scientific Research (Dr. Gernot Pomrenke, program manager) in partnership with the Air Force Research Laboratory Nanoscience and Technology Strategic Technology Team.

#### Nano-Jet Micro-Thrusters for Space Propulsion

**Accomplishment:** A new micro-thruster using a nano-jet spray of ionic liquid propellants has been developed and successfully validated. These electro-spray nano-jets produce nanometer-sized vapor droplets that give a ten-fold improvement in micro-thruster propulsion efficiency.



**Impact:** Electro-spray nano-jets enable the miniaturization of conventional electric thrusters, producing a new electric micro-thruster. Nano-jet micro-thrusters are essential for long-term precision positioning of satellites and for future AF nano-satellite missions. They also give improved mission flexibility by significantly reducing the lift-off mass of next-generation spacecraft, or by increasing mission lifetimes by roughly an order of magnitude at equivalent launch weight. These nano-jet micro-thrusters have been incorporated in upcoming NASA space missions as a transition path toward military applications.

**Motivation and Approach:** AF satellite missions require a choice between chemical propellants, which give very high thrust for relatively

short periods of time, or electric propulsion, which gives low thrust for very long periods of time. Electric propulsion is the preferred approach for long-duration satellite maneuvers and for miniaturized satellites (nano-satellites). However, present plasma electric thrusters become much less efficient upon miniaturization, forming a significant barrier to future AF satellite missions. Electro-spray nano-jets enable electric propulsion that can be miniaturized without loss of efficiency. The nanojet micro-thrusters developed here use ionic liquid propellants that give significant power savings, greatly improving the miniaturization potential and enabling a dramatic extension of propulsion efficiency. As a result of these efforts, nano-jet micro-thrusters using an ionic liquid propellant will be used for high precision positioning of an upcoming NASA satellite mission.



**Team:** This research was led by Dr. Yu-Hui Chiu (Space Vehicles Directorate) and Dr. Tommy Hawkins (Propulsion Directorate), in collaboration with Prof. Uzi Landman (Georgia Institute of Technology), Prof. Manuel Martinez-Sanchez (Massachusetts Institute of Technology) and Prof. Juan Fernandez de la Mora (Yale University). The research was funded by the Air Force Office of Scientific Research (Dr. Michael Berman and Dr. Mitat Birkan, Program Managers).

### DNA Nano-Taggants for Covert Watermarking,

#### Tracking and Communication

**Accomplishment:** A simple, compact, low-cost method to produce, apply and detect DNA-tagged items was developed. These detection methods can provide rapid, reliable detection of DNA taggants in the field.

**Impact:** DNA taggants are an information assurance technology for objects with restricted access that verifies access and gives effective, covert tamper detection. They also provide watermarking to validate authenticity of sensitive documents and to verify human assets. For intelligence operations, taggant-encoded information can provide covert communications and the mapping of networks of personal contacts.

Motivation and Approach: DNA taggants are distinctive combinations of synthesized DNA that can be applied to surfaces, objects, materials or personnel. Like nanometer-sized barcodes, they enable the origin of the tagged article to be verified, traced and monitored for movement. DNA taggants consist of molecules that are each typically 3 nanometers in diameter by 10 nanometers long, and so are extremely discreet and difficult to detect by ordinary methods. Current DNA taggant technologies require the tagged sample to be sent to a laboratory, where the time to verify a DNA signature is on the order of hours. In military and intelligence applications, removing the article of interest to a testing facility is unacceptable and much shorter detection times are needed.

This research developed a technology to create unique libraries of DNA taggant sequences. Methods to apply or disperse the taggants were developed, and the adherence and viability on a variety of surfaces was demonstrated. The taggants were shown to be transferable between different surfaces, such as keyboards, currency, data storage media and painted surfaces, and were made more robust on surfaces containing other substances such as polymers. Two techniques for rapid, portable detection of DNA taggants were developed. Both methods take just minutes, and a positive detection is easily viewed by a color change. The detection kit requires only a 5 millimeter square absorbant pad containing the reagents that carry out the detection reactions. These taggants were verified to be nontoxic for human handling.

**Team:** The research was conducted by Prof. John Reif (Eagle Eye, Inc.), with contributions from Prof. Tom Lebean (Duke University) and Prof. Hao Yan (Arizona State University). Dr. Thomas Renz at the Information Directorate gave guidance on relevant military applications. The research was funded by a Small Business Innovation Research project from the Information Directorate.

#### Nano-Aluminum Alloy to Replace Titanium in Liquid Rocket Engines

**Accomplishment:** A nanoparticle strengthened cast and wrought aluminum alloy with a strength-to-weight up to 30% higher than high purity Ti-5Al-2.5Sn has been developed. A full scale impeller of this alloy surpassed the properties required for a revolutionary two stage liquid hydrogen turbopump.



**Impact:** This alloy enables a revolutionary two stage liquid hydrogen turbopump that achieves major objectives of the Integrated High Payoff Rocket Propulsion Technology (IHPRPT) Initiative for dramatic increases in thrust-to-weight, reliability and affordability of liquid rocket engines for improved access to space. Additional applications are being pursued with industrial partners, including turbopump housings and large pipes in liquid rocket engines, aircraft wheels and automotive parts.

*Motivation and Approach:* Increasing the strength-to-weight of liquid hydrogen turbopump impeller alloys offers the most significant opportunity to improve thrust-to-weight, reliability and affordability of liquid rocket engines. This allows increased impeller speed, giving higher compression and reducing the number of impeller stages from three to two, giving dramatic decrease in weight, volume and cost. The titanium alloys currently used are expensive and have little potential for higher strength-to-weight. Almost all other metal alloys are embrittled in liquid hydrogen, are heavy, or have poor ductility at the operating temperature of -425 degrees Fahrenheit. Current commercial aluminum alloys satisfy all impeller requirements except strength-to-weight.

Existing aluminum alloys were modified with up to 0.8% by weight of elements that combine with aluminum during controlled heat treatment to form nanometer-sized strengthening particles. Strengthening becomes increasingly potent as the size and spacing between the particles approaches nanometer dimensions. About 0.5-0.9% by volume of strengthening particles that are 5-30 nanometers in diameter and 50-150 nanometers apart give a strength-to-weight in these new aluminum alloys that is up to 30% higher than the high purity Ti-5AI-2.5Sn titanium alloy currently used for liquid hydrogen impellers. Processing and manufacturing of billets up to 20" in diameter was established. A full-scale impeller was designed, manufactured and successfully spin-tested, exceeding the rotation speed needed for a revolutionary two-stage turbopump.



**Team:** This research was led by Dr. Oleg Senkov at UES, Inc., with contributors in the Materials and Manufacturing Directorate and the Propulsion Directorate. The program was managed by Dr. Kevin Kendig at the Materials and Manufacturing Directorate. Funding was provided by a Small Business Innovation Research program, from IHPRPT, from the Air Force Office of Scientific Research (Dr. Brett Connor, Program Manager) and from the Materials and Manufacturing Directorate. Industrial partners included Pratt and Whitney Rocketdyne (formerly Boeing Rocketdyne), Wagstaff Engineering, Wyman-Gordon and Universal Alloy Corporation.

### Nano-Composite Coatings for F-35 LiftFan and RL-10 Rocket Engine Turbopump

**Accomplishment:** Composite coatings combining nanocrystalline particles with an amorphous metal matrix have been developed that give an order of magnitude decrease in component wear, good corrosion prevention in salt environments, and enable system operation under demanding lubricant starvation requirements.



**Impact:** This advancement satisfies operational requirements for endurance and reliability in liftfan gears and bearings of the short takeoff-vertical landing(STOVL)F-35aircraft. Conventional coatings are unable to satisfy the full range of operation conditions, placing successful accomplishment of mission requirements at risk. This advanced coating is being certified for F-35 aircraft gears and is also being validated in component-level testing for gears in the RL-10 liquid rocket engine turbopump.

**Motivation and Approach:** Gears and bearings in jet engines and rocket turbopumps must perform under difficult conditions that include high contact stresses, high wear conditions and corrosive environments. The F-35 STOVL LiftFan adds the demanding requirement of continued engine operation after 60 seconds of unlubricated runtime, which could not be satisfied by any previously available coating. This new class of

wear resistant nano-composite coatings has an unusual combination of high hardness that exceeds ceramic materials, and fracture strength similar to that of tough metal alloys. These properties result from the combination of 3-5 nanometer grains of very hard carbides or oxides embedded in an amorphous metal matrix. The material design was further enhanced by introducing coating interfaces with corrosion prevention layers and by using carbon in the composite matrix to reduce friction during unlubricated operation. Subsequent applied research and process development is establishing these nano-composite coatings for use in F-35 STOVL propulsion system components and RL-10 liquid rocket engine turbomachinery, where component-level testing is now underway.



Team: These coatings were conceived and developed under the leadership of Dr. Andrey Voevodin, with significant contributions from Dr. Jeff Zabinski, Dr. John Jones and Benjamin Phillips, (all at the Materials and Manufacturing Directorate), and from Dr. Chris Muratore (Universal Technologies, Corp.) and Dr. Jiaunjun Hu (University of Dayton Research Institute). Funding was provided by the Air Force Office of Scientific Research (Maj. Jennifer Gresham, Program Manager). Small Business Innovation Research programs with Arcomac Surface Engineering, Inc. and Tribologix, Inc. developed processes to apply these coatings, which are being validated by component testing by the Rolls-Royce Corporation (for the F-35 LiftFan) and Pratt and Whitney (for the RL-10 rocket engine).

#### First Electrically Pumped Semiconductor Room-Temperature Terahertz Radiation

**Accomplishment:** The first room-temperature electrically pumped semiconductor source of Terahertz radiation was demonstrated using quantum cascade semiconductor lasers. Beams with power levels sufficient for a number of applications were demonstrated.



**Impact:** Terahertz imaging and sensing is a promising but relatively new technology for imaging of concealed weapons, detecting chemical and biological agents through sealed packages and spotting defects within materials. The devices developed and tested here are an important first step toward requirements for compact, portable and tunable sources of terahertz rays.

**Motivation and Approach:** The ability of Terahertz rays (T-rays) to penetrate efficiently through paper, clothing, cardboard, plastic and many other materials makes them ideal for imaging of concealed weapons, detecting chemical and biological agents through sealed packages, seeing tumors without harmful side effects, and spotting defects within materials such as cracks in the space shuttle foam. Existing terahertz devices require cryogenic cooling, greatly limiting their applications by increasing system size and complexity and restricting portability. There were previously no compact terahertz devices that could operate at room temperature, or even with simple thermoelectric cooling. To overcome these serious limitations, a speciallydesigned room temperature mid-infrared quantum cascade laser was built and tested. Quantum cascade lasers consist of alternating layers of semiconductor materials that are a few nanometers thick. These commercially available lasers are small (a few millimeters in length) and the wavelength of the emitted laser light can be selected over an extremely wide spectral range by choosing the thickness of the semiconductor layers. The laser developed here was designed to generate light at two frequencies simultaneously, which then mix in the active region of the device to emit coherent light at their difference frequency of 5 Terahertz. Beams can be produced with several hundreds of nanowatts of power at room temperature and microwatts of power at temperatures easily achievable with commercially available thermoelectric coolers, which is sufficient for a number of applications.



**Team:** This research was conducted by Prof. Federico Capasso and Dr. Mikhail Belkin at Harvard University, Prof. Alexey Belyanin and Feng Xie at Texas A&M University and Prof. Jérôme Faist, Milan Fischer and Andreas Wittmann of the Institute of Quantum Electronics, ETH, Zürich, Switzerland. This research was funded in part by the Air Force Office of Scientific Research (Dr. Gernot Pomrenke, Program Manager).

#### Nano-Additive Demonstrates Potential for JP-900 Fuel

**Accomplishment:** A new fuel additive based on reactive metal nano-particles has demonstrated the ability to deoxygenate kerosene-based fuels at controlled temperatures.



**Impact:** Development of a kerosene-based aviation fuel that can be heated to 900 degrees Fahrenheit (JP-900) is an enabling technology for Mach 4 flight and directly supports the Long Range Strike fighter program, the Versatile, Affordable Advanced Turbine Engine (VAATE) program and the National Aerospace Initiative. This accomplishment validates a new approach with the potential to achieve this requirement.

Motivation and Approach: Onboard aviation fuels are a primary heat sink used to cool engine components, avionics and electronics, munitions bays, and structural parts subjected to aerodynamic heating during supersonic flight. Standard fuels begin to degrade above 325 degrees Fahrenheit by interaction with small amounts of oxygen dissolved in the fuel. Current additives increase the maximum fuel temperature to 425 degrees Fahrenheit, above which the additives lose effectiveness or begin to break down. Many aircraft, including the F-22 and B-2, have significant thermal deficits that limit operational capability by heating the fuel above these temperatures. Summertime thermal aborts are common during pre-flight systems checks at ground idle, and the duration of supersonic flight is restricted. The maximum temperature

capability of de-oxygenated kerosene-based fuels is 900 degrees Fahrenheit. This JP-900 class fuel provides a solution to these thermal deficit issues and is an enabling requirement for flight at Mach 4 and above. There are currently no approaches that give this capability.

Reactive metal nano-particles less than 100 nanometers in diameter were developed in this work as fuel additives. The metal nano-particles react with dissolved oxygen to remove it from the fuel. The small size ensures that the particles can be suspended easily for compatibility with fuel system pumps and filters, and the very high surface area of the nano-particles enhances chemical reactivity. A molecular shell less than a few nanometers thick is deposited on the metal nano-particle to control the temperature at which deoxygenation occurs, preventing early or unwanted reaction, and giving maximum effectiveness. This coating can also be tailored to improve the dispersion of the core-shell nano-particles in the fuel. Core-shell nano-particles have been designed and produced, and their ability to deoxygenate fuel at a controlled temperature has been established. These nano-particle additives have demonstrated thermal stability equal to the current state of the art, with the goal of continued development being to achieve fuel heat sink temperatures up to 900 degrees Fahrenheit.



**Team:** This research is being conducted at the Propulsion Directorate by Dr. Christopher Bunker and Dr. Elena Guliants (University of Dayton Research Institute). Funding was provided by the Air Force Office of Scientific Research (Dr. Julian Tishkoff, Program Manager) and the Propulsion Directorate.

### Processing of Explosive Formulations with Nano-Aluminum Powder

**Accomplishment:** A processing methodology was developed to incorporate a high volume fraction of nano-aluminum powder into moldable munitions formulations.



**Impact:** Munitions enhanced with nanoaluminum powder are being developed to give performance and lethality enhancements in miniaturized munitions needed for the reduced volume of advanced aircraft munitions bays and for weaponization of unmanned air vehicles (UAVs). Munitions using nano-aluminum powder may give improved lethality by improving the airblast and the shrapnel accelerating capability over conventional formulations.

**Motivation and Approach:** Aluminum powders that are tens of microns in diameter are used to increase the energy density in conventional munitions and solid rocket fuels. Oxygen reacts with the powder surface, giving off significant heat but forming a barrier to further oxidation, so that

only partial reaction is achieved. Nano-particles have much higher surface area than conventional powders. The reaction rate of nano-powders can be controlled by adjusting the nano-particle diameter, giving tailorability for optimized airblast and for fragment formation and acceleration. Higher power density is provided by more complete reaction and higher reaction rate of nano-aluminum powders. The high surface area is wetted by binders used to make conventional munitions formulations processible, increasing the viscosity and making blending and casting difficult. Only a few percent by volume of nano-aluminum powder could previously be added to munitions formulations, forming a major barrier to the development, production and characterization of advanced munitions with significant additions of nano-aluminum powders.

processing methodology has been A new developed to overcome this barrier. A conventional castable munitions formulation, which typically has a viscosity similar to honey, is thinned with a solvent so that the nano-aluminum powder can be added. The solvent also desensitizes the formulation so that it is safer to handle during processing. The solvent vaporizes during blending, leaving a granular formulation with the consistency of brown sugar that can be easily molded to fill munitions containers. Only 6% by volume of binder is needed, and up to 50% by volume of nano-aluminum powder can now be added, compared to only a few percent using previous techniques. An order of magnitude improvement in density control is achieved, giving better reproducibility of blast characteristics. Extension of this processing methodology to add nano-aluminum powders to conventional munitions formulations is being pursued at industrial partners, including ATK and Savannah River National Laboratory. Performance testing is underway.

**Team:** This research was accomplished at the Munitions Directorate by Chad Rumchik.

#### Nano-Column Fabrication for Gallium Nitride Radio Frequency Electronics

**Accomplishment:** Gallium nitride (GaN) single crystal substrates with defect densities up to 10,000 times lower than the current state-of-the-art were made using nano-columns as a base layer. The growth technique was demonstrated and characterized in a laboratory environment.



**Impact:** GaN devices offer significant improvements in elevated temperature operation, resistance to radiation damage, structural integrity and high frequency operation over existing silicon or gallium arsenide semiconductor technologies. These capabilities are essential for radio frequency electronics used for electronic warfare, radar, and communications applications.

Motivation and Approach: State-of-the-art semiconductors used for radio frequency (radar and microwave) electronics are susceptible to radiation damage from electronic warfare countermeasures and in space missions, can fail at elevated temperatures generated by high power devices, and are susceptible to damage from mechanical vibration. GaN offers significant improvements in these environments, and also operates at higher frequencies, giving more efficient data transfer and more secure communications. Like existing semiconductors, GaN must be grown as single crystals for high quality electronics. Despite more than a decade of research, techniques to grow GaN single crystals give a high number of defects that significantly degrade performance, reliability and lifetime, forming a significant barrier to application of this technology.

This accomplishment validates the critical first step for producing large, high quality single crystal GaN crystals with defect densities 10,000 times lower than currently possible. A layer of aluminum nitride less than 150 nanometers thick is deposited on commercially available silicon or sapphire single crystal wafers. GaN nano-columns 100 nanometers in diameter with very low defect densities are grown on the aluminum nitride using molecular beam epitaxy, a commercial fabrication process, to carefully control the nano-column size, orientation and spacing. The vertical nano-column growth is transformed to lateral growth by switching to a second commercial processing technique, metal-organic chemical vapor deposition. This lateral growth produces GaN plateaus that are up to 10 microns in diameter and have the same low defect density as the underlying nano-columns. Joining plateaus to form a very large single crystal substrate is the next step and is currently underway. A path toward foundry-class electronics fabrication is being pursued through collaboration with Kyma Technologies.



**Team:** This work was performed by Dr. John Albrecht (Sensors Directorate), Dr. Kent Averett (Materials and Manufacturing Directorate) and Prof. Chih-Chung Yang (National Taiwan University). Funds were provided by the Air Force Office of Scientific Research through in-house research tasks (Dr. Don Silversmith, Program Manager) and through the Taiwan Nanoscience Initiative (Dr. Harold Weinstock, Dr. Don Silversmith and Dr. Jim Chang, Program Managers). Kyma Technologies is funded through the Small Business Innovation Research (SBIR) program.

#### Photon-Plasmon-Electron Conversion Enables A New Class of Imaging Cameras

**Accomplishment:** The world's smallest array of imaging pixels was conceived and created. A device was built and tested to demonstrate this new imaging approach.



Impact: High resolution, multi-spectral and polarimetric imaging systems are essential for intelligence, surveillance and reconnaissance missions. The present accomplishment demonstrates a new imaging approach that offers these capabilities at significantly reduced volume, weight and cost relative to conventional systems. This provides mission enhancement for conventional aircraft, and may give an enabling new capability for platforms with limited payloads, such as unmanned air vehicles.

**Motivation and Approach:** The size, weight and cost of imaging cameras are important considerations for conventional air vehicles, and are enabling considerations for platforms with significant restrictions on payload weight and volume such as

unmanned air vehicles (UAVs). The size, weight and cost of imaging systems increase dramatically with the size of the imaging chip. High resolution cameras require more pixels, increasing the detector size. The imager pixel size is currently limited by the physics of light diffraction to 2.0 microns for visible light, thus limiting the potential to reduce the size of imaging cameras. Improved target identification and the ability to distinguish between manmade and natural features requires simultaneous signal collection from more than one wavelength of light (multi-spectral imaging) or from polarized signals (polarimetric imaging), also significantly increasing the imager system size. These capabilities are currently difficult to incorporate into unmanned air vehicles due to size and weight restrictions.

The present accomplishment conceived and demonstrated a new detector imaging approach that converts photons from an incoming optical signal into surface plasmon waves (as sound waves are produced by oscillating densities of air molecules, plasmons are quantized oscillations of the electron gas in a metal). The plasmon waves are formed in a metal film that is typically less than 100 nanometers thick bonded to a semiconductor base, and they are collected by a slit in the metal film, where their energy is focused to produce electron/hole pairs in the semiconductor that give a measurable electrical signal. The plasmon has a wavelength shorter than that of the incoming light, and so the diffraction-limited minimum pixel size is also reduced. This phenomenon was exploited here to demonstrate an imager with a pixel size of 1.3 microns. Different polarization signals may be produced from the same imaging chip by fabricating different slit orientations, and multi-spectral signals can be produced by fabricating an imaging chip with several different slit sizes. This accomplishment provides a decrease in detector size of at least 50% relative to existing technology at equivalent resolution.

**Team:** This research was conducted by Dr. Ravi Verma and Dr. Joe Lee (Tanner Research), and by Prof. Mark Brongersma and Justin White (Stanford University). The research was funded by the Air Force Office of Scientific Research (Dr. Gernot Pomrenke, Program Manager).





#### Nano-Particle Lubricant Produced by Biosynthesis

**Accomplishment:** Biological templates were successfully used to direct the synthesis and assembly of bimetallic nano-particles. The performance of these nano-particles was demonstrated as a conductive lubricant in microelectro-mechanical systems (MEMS) electrical switches at high current with no failure through one million hot-switching cycles.



Impact: The present accomplishment demonstrates а simple, flexible real-time manufacturing capability that can produce a wide array of engineered nano-particles in the field in response to locally identified specific threats. Potential applications include dechlorination of drinking water, decontamination of nerve agents and electrically conductive lubricants for microelectro-mechanical systems (MEMS).

**Motivation and Approach:** Nano-particle catalysts are currently used against a wide range of chemical agents, including dechlorination of drinking water, decontamination of nerve agents and environmental cleanup. However, these nano-particles must be tailored for a specific agent, and must currently be produced in a controlled manufacturing environment remote from the battlespace, dramatically increasing the response time and logistic requirements. The size, shape and composition of engineered nano-particles

must be carefully controlled during manufacture to give the needed optical, electronic, catalytic and mechanical properties. It has recently been shown that biological molecules, such as peptide chains containing up to 20 selected amino acid molecules, can be used to synthesize engineered nanoparticles. This approach uses simple and flexible chemistry techniques that can be easily applied in the field.

In the present accomplishment, two separate peptide chains were connected, forming a new biological template to synthesize hybrid nanoparticle structures. The first peptide chain directs the nucleation and growth of a metal nano-particle from a liquid solution. When the nano-particle grows to a specified size between 8 nm and 25 nm, the peptide chain coats the nano-particle surface. A second type of metal ion was then dissolved in the solution, and the second peptide chain directs the growth of smaller nano-particles (1-2 nm) that are attached to the larger nano-particle through the peptide chain. These hybrid bimetallic nano-particles have new or enhanced properties relative to single nano-particles, and are highly desired for a number of applications. They were shown to be twice as efficient as traditional nano-particle catalysts and use as a conductive lubricant for MEMS electrical switching devices was demonstrated in this work. Many other uses are envisioned, such as an enabling fuel cell technology.



**Team:** Dr. Rajesh Naik, Dr. Andrey Voevodin, Dr. Steve Patton and Dr. Joseph Slocik of the Materials and Manufacturing Directorate were responsible for the technical innovation leading to this accomplishment.

#### **Polymer Nano-Layer Coatings for Optical Applications**

**Accomplishment:** A deposition process enabling precise nanometer-scale thickness control in functional polymers has been demonstrated. Complex nano-structured polymeric thin film coatings of plasma polymerized monomers with unique optical properties are difficult to prepare by any other technique, but are now possible and have been demonstrated with this process.



**Impact:** Multi-layer optical coatings are used wherever the transmission, reflectance or absorption of light is required to achieve system functions, including optical sensors, aircraft canopies, display panels, heads-up displays, pilot glasses and helmet faceshields. Conventional optical coating properties are limited by the relatively small number of inorganic compounds that have desirable optical properties. This accomplishment greatly expands the range of properties that can be produced in optical coatings by enabling production of polymer-based coatings with the adhesion, durability and processibility necessary to achieve system functions.



Motivation and Approach: High performance optical coatings typically consist of inorganic materials that are relatively heavy and expensive and have a limited range of desirable optical properties. By comparison, polymer materials are less costly, much lighter and offer a much broader range and tailorability in optical properties. However, previously available deposition processes produce rough polymer films with defects that degrade optical properties, have poor durability and adhesion to the substrate, and often have poor chemical, thermal and environmental stability. A plasma-enhanced chemical vapor deposition process was modified in this accomplishment to overcome these deficiencies while retaining nano-scale control of the optical thickness. This new process technique can also polymerize organic monomer compounds that previously could not be used, greatly increasing the palette of candidate optical materials and properties. Single layer, multilayer, and graded refractive index nano-structured polymeric-thin film coatings for photonic applications have all been fashioned from organic monomers using this plasma enhanced chemical vapor deposition capability.

**Team:** This work was led by Dr. Tim Bunning in the Materials and Manufacturing Directorate. Funding came from the Air Force Office of Scientific Research (Dr. Charles Lee, Program Manager).



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#### Nano-Crystalline Zinc Oxide for High Performance Thin Film Transistors

**Accomplishment:** Zinc oxide thin film transistors were produced to give the highest performing thin film transistors to date. It was shown for the first time that thin film transistors can be used for microwave applications.

**Impact:** These results give initial validation that thin film transistors can be used for high performance electronics, enabling integration with other electronic and mechanical systems to give improved reliability and reduced weight, volume and cost. New capabilities, such as application of thin film transistors to microwave devices, are now feasible. The added function of optical transparency enables an optical sensor to be placed on top of a radio frequency (microwave and radar) sensor, improving target location and identification and solving physical space issues in systems where volume and weight are severely limited, such as satellites and unmanned air vehicles (UAVs).

Motivation and Approach: Conventional solid state transistors are typically produced on semiconductor single crystals that are expensive and restricted to sizes less than a few hundred millimeters in diameter. Thin film transistors are far less expensive since they can be produced on any substrate and can be made in dimensions exceeding 1 meter. They can be integrated with other devices and can be deposited on thin films that are flexible and conformal. Current thin film transistors have poor electronic performance, including low current densities and low operation frequencies, and rely on rare elements such as indium. Thin film transistors are a widely-used enabling technology for liquid crystal displays (LCDs), but their poor electronic characteristics severely limits other applications that require high performance, high speed capabilities.

In this work, careful control of the structure and processing of nanocrystalline zinc oxide films have produced dramatic improvements in thin film transistor performance. Magnetron sputtering and pulsed laser deposition, both commercial fabrication techniques, are used with post-deposition heat treatment to optimize the nanocrystalline grain size and defects of the deposited transistors. Current densities more than 1000 times higher than previous values have been produced, and on/off current ratios 1 million times higher than previously possible have been achieved. An operation frequency of 500 Megahertz has been demonstrated with nanocrystalline zinc oxide thin film transistors on a gallium arsenide substrate, giving a dramatic increase in operation frequency and demonstrating for the first time feasibility for microwave signal amplification. These are record values for any thin film transistors. When doped (alloyed) with aluminum, these zinc oxide thin film transistors can be made optically transparent, opening up a new range of applications.



**Team:** The research was led by Dr. Burhan Bayraktaroglu and Dr. Kevin Leedy at the Sensors Directorate, with funding from the Air Force Office of Scientific Research (Dr. Kitt Reinhart, Program Manager).

#### **Quantum Cascade Laser Nano-Antenna for Future Identification of Biological Threats**

**Accomplishment:** A simple, compact approach to concentrate infrared laser light to a spot size of roughly 100 nanometers was conceived and demonstrated. This may enable chemical mapping with a spatial resolution that is 50-100 times better than conventional infrared microscopes.

**Impact:** Among the long term applications suggested by the high spatial resolution of this device is the identification of biological threats such as spores, bacteria and cells. This device also suggests the possibility of broadband spectral coverage, which might be useful to identify complex, heavy molecules such as those in toxic chemicals, explosives, and drugs.



Motivation Approach: Biological and materials have specific absorption profiles in infrared light, and so they can be uniquely identified with a chemical composition map obtained by scanning a spot of infrared light and measuring the transmitted light. A spatial resolution of one micron or less is needed to resolve spores and bacteria and to identify separate features of cells, but the spatial resolution of infrared microscopes is limited by the physics of optics to no less than the wavelength of the infrared light used, about 4 to 10 microns. Additionally, accurate chemical determination requires more than one wavelength of infrared light, but current infrared microscopes, especially those with the best spatial resolution, cannot provide the needed wavelength coverage.



The present innovation deposits a nano-antenna on the face of a quantum cascade laser to overcome a major obstacle of infrared microscopes for chemical mapping with high spatial resolution. Quantum cascade lasers consist of alternating layers of semiconductor materials that are typically a few nanometers thick. These lasers are small (a few millimeters in length), can be designed to produce light over the full infrared spectrum, and are commercially available. The nano-antenna consists of two aligned gold rectangles, each having a length about half the wavelength of the infrared light, separated by a gap of roughly 100 nanometers. The gold nano-rods concentrate the laser light in the antenna gap to produce an intense, localized light source that is 50-100 times smaller than the typical spot size in conventional infrared microscopes. Submicron resolution of biological samples may now be possible with this quantum cascade laser/ nano-antenna assembly.

**Team:** This research was led by Prof. Federico Capasso, with contributions from Prof. Kenneth Crozier, Dr. Mikhail Belkin and Dr. Laurent Diehl (all at Harvard University), and from Dr. David Bour, Dr. Scott Corzine, and Dr. Gloria Höfler, formerly with Agilent Technologies. This research was funded in part by the Air Force Office of Scientific Research (Dr. Gernot Pomrenke, Program Manager).



#### Uncooled Infrared Detector Made Possible with Controlled Carbon Nano-Tube Array

**Accomplishment:** The processing of a highly ordered array of highly uniform carbon nanotubes with an electronic-grade junction to a silicon semiconductor substrate was developed. Dual band infrared detection was demonstrated in uncooled operation for the first time in these devices.



**Impact:** This new material system gives a broadly enabling platform for future multi-spectral infrared and biochemical sensing applications. Multi-band detection can be achieved over a broad spectral range from near infrared to far infrared by building arrays with several distinct nanotube diameters, replacing several conventional detectors with a single detector array. This capability is important for miniaturization and for providing new sensing capabilities in platforms with limited payload such as satellites and unmanned air vehicles (UAVs).

**Motivation and Approach:** Carbon nanotubes are a molecular form of carbon that can be visualized as a planar hexagonal net of carbon atoms (a graphene sheet) that has been rolled and joined at the edges to form a tube. Carbon nanotubes are typically less than a few tens of nanometers in diameter and up to several millimeters in length, and can have a hemispherical cap on one or both ends. Carbon nanotubes have exceptional electrical, thermal, chemical and mechanical properties that motivate and enable completely new functions and capabilities, including structural components

with superlative strength-to-weight; microscopic electronic circuits; sensors and transmitters with unique characteristics; and controlled drug delivery. A major obstacle to the realization of nanotube capabilities has been the lack of approaches for the mass production of high quality and high uniformity carbon nanotubes, and for organizing them into useful architectures.

The present work develops the template-assisted chemical vapor deposition method to produce a highly ordered array of high quality carbon nanotubes of controlled diameter, length and spacing. This process deposits a uniform, high purity aluminum film on a silicon semiconductor substrate. Precision anodization transforms the aluminum to aluminum oxide and forms a uniform nano-pore array in the aluminum oxide that stops precisely at the silicon interface. A nano-particle of iron is deposited at the bottom of each nano-pore and a carbon nanotube is subsequently grown at high temperature on each iron nano-particle. An electronic-grade heterojunction contact is formed between the carbon nanotubes and the silicon semiconductor substrate. This unique architecture gives a broadly enabling base technology for a range of applications. The first uncooled dual-band infrared heterojunction detector was demonstrated in this on-going effort. Conversion of electromagnetic radiation to heat by the carbon nanotube array has been conceived and is being explored as a possible approach for protection from electromagnetic pulses.

**Team:** This research was conducted by Prof. Jimmy Xu and his research team at Brown University. Collaborators include Dr. Gail Brown (Materials and Manufacturing Directorate), Dr. Dave Cardimona and Dr. Dan Huang (Space Vehicles Directorate) and Dr. Richard Osgood (Army Natick Center). Funding was provided by the Air Force Office of Scientific Research (Dr. Hugh DeLong and Dr. Gernot Pomrenke, Program Managers) and by the Army Research Office (Bill Clark, Program Manager).

### The Environmental, Safety and Occupational Health of Nanomaterials at the Air Force Research Laboratory

Nanomaterials are not new. They occur in nature – the water repelling properties of lotus leaves, the stickiness of gecko feet and information storage in DNA molecules all have nanomaterial origins. Nanomaterials have long been used unknowingly, for example to control the colors in medieval stained glass and to give Damascus steel its unique properties. And nanomaterials are now used extensively in intentionally engineered systems that include circuit features in solid state electronics, high-strength aluminum-based structural metals and water repellent textiles.

Recent developments have generated a degree of apprehension concerning potential environmental, safety and occupational health (ESOH) risks associated with new, engineered nanomaterials. This is particularly true for discrete nano-particles, which may be dispersed and taken up in the human system and may interact with living cells. The production and manipulation of discrete nano-particles is a relatively recent capability. Few controlled studies have been conducted at the cellular level to establish if exposure risks exist, and to establish sound protocols for their safe production, handling, use, and disposal while still allowing the materials to be used for maximum benefit. The great variety of physiochemical properties such as size, shape and surface chemistry of nano-particles makes safety assessment a challenging problem.

AFRL is providing important leadership in efforts to address this issue. AFRL scientists are conducting focused research to establish the possible effects of nano-particle exposure on biological systems. To discuss potential toxicity, health, and environmental issues in the Department of Defense (DoD) community, Dr. Saber Hussain of the 711th Human Performance Wing, Human Effectiveness Directorate, organized and led the first Air Force Workshop on Biological Interaction of Engineered Nanomaterials with support from the Air Force Office of Scientific Research (AFOSR) and the Aeronautical Systems Center (ASC). This Workshop brought together participants from industry, academia and Government agencies, including the Environmental Protection Agency and the National Institute for Occupational Safety and Health, to communicate and discuss current controls associated with the use of nanomaterials. AFRL scientists are key members of the DoD Nanomaterials ESOH Working Group. In coordination with the DoD Emerging Contaminants Governance Board, this Working Group provides technical, policy and legal information relating to the safety and health issues associated with engineered nanomaterials. AFRL also provided important input to the ESOH policy letter, signed by the Under Secretary of Defense for Acquisition, Technology and Logistics, that reinforces responsibilities and provides information and procedures for managing ESOH risks of engineered nanomaterials in DoD research, acquisition, operations, and support. These ongoing efforts establish strong AFRL leadership in the science and safety of engineered nanomaterials for the Air Force and for the Department of Defense.



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#### Air Force Research Laboratory

LEAD | DISCOVER | DEVELOP | DELIVER

The Air Force Research Laboratory (AFRL) is the Air Force's only organization wholly dedicated to leading the discovery, development, and integration of warfighting technologies for our air, space and cyberspace forces. AFRL traces its roots back to the vision of early airpower leaders who understood science as the key to air supremacy. The passionate commitment of our people to realize this vision has helped create the world's best air, space and cyberspace force.

#### Mission

AFRL's mission is leading the discovery, development and integration of affordable warfighting technologies for America's aerospace forces. It is a full-spectrum laboratory, responsible for conceiving, planning and executing the Air Force's science and technology program. AFRL leads a worldwide government, industry and academia partnership in the discovery, development and delivery of a wide range of revolutionary technologies. The laboratory provides leading-edge warfighting capabilities keeping our air, space and cyberspace forces the world's best.

#### **Personnel and Resources**

The lab employs approximately 5,400 government people, including about 1,300 military and 4,100 civilian personnel. It is responsible for the Air Force's science and technology budget of nearly \$2 billion including basic research, applied research, advanced technology development and an additional \$1.7 billion from AFRL customers.

#### Organization

AFRL accomplishes its mission through nine technology directorates located across the United States, through the Air Force Office of Scientific Research, and with the support of a central staff. The directorates are: Air Vehicles Directorate, Directed Energy Directorate, Human Effectiveness Directorate, Information Directorate, Materials and Manufacturing Directorate, Munitions Directorate, Propulsion Directorate, Sensors Directorate, and Space Vehicles Directorate.

#### History

The laboratory and its predecessors have led more than 80 years of critical research efforts for the Air Force and the Department of Defense. Its technology breakthroughs can be found in all of today's modern aircraft and weapons systems, including the B-2 bomber, C-17 airlifter and the F-22 fighter. It also contributed to significant advancements in modern communications, electronics, manufacturing, and medical research and products.





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