NEXT GENERATION NANOTECHNOLOGY ASSEMBLY FABRICATION METHODS: A TREND FORECAST

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Abstract

Today, the continued success of many industries, especially the microelectronics industry, relies upon the ability to fabricate structures with nanometer precision. The efforts toward developing nanometer scale fabrication methods fall loosely into two fields. One field seeks to extend the current planar, deposit-pattern-etch paradigm used for complementary metal oxide semiconductors (CMOS). This is a top-down approach. The other seeks new techniques to assemble structures without handling individual particles—self-assembly. These techniques take a bottom-up approach.

The fundamental limits of the materials used in the planar CMOS process, which has been the basis for the semiconductor industry for the past 30 years are now being reached. This is driving industry to fund research to find new fabrication methods. The thesis of this paper is that as new fabrication methods are mastered in the quest to continue advancement in computer processing, these techniques will propagate to other applications with the potential to threaten US national security interests.

CHAPTER 1

INTRODUCTION

"The revolutionary Feynman vision of a powerful and general nanotechnology, based on nanomachines that build with atom-by-atom control, promises great opportunities and, if abused, great dangers."
K. Eric Drexler, Foresight Institute.[1]

What is Nanotechnology?

Nanotechnology is an often misunderstood term. Say the word, and you are likely to elicit various conceptions from complete ignorance of the term to the fear of a science fiction type mass assembler that threatens the world.[2] The term has come to mean different things to different people.

"Nano" is a prefix meaning one-billionth. In distance, a nanometer is one billionth of a meter. As illustration, a human hair is 100,000 nanometers (nm) in width. A red blood cell measures approximately 5,000 nm across. Ten hydrogen atoms, lined up side by side, if they were touching, would form a line roughly one nanometer in length. What confuses the situation is that some define nanotechnology as anything below the size of one micron or 1000 nanometers.[3] This definition is often used in mass media, but it is not scientifically accurate. The definition used in this paper, and the one used by the National Nanotechnology Initiative (NNI) group, defines nanotechnology as a technology involving, at a minimum, all of the following: research at the 1 to 100 nm range; creating and using structures that have novel properties because of their small size; and the ability to control or manipulate at the atomic scale.[4]

Discussion of nanotechnology can quickly become complex as a full analysis involves advanced chemistry, biology, physics, computer science, and engineering. The properties of nano-scale materials are governed by laws of quantum physics, causing materials to display properties and characteristics that would be considered by the laws of classic Newtonian physics. It is these intermolecular forces which cause nanotechnology to be both a vexing research problem, and yet have enormous potential. While the science of nanotechnology can be highly complex, this report strives to remain at a layman's level and thus avoids the complex equations and physics involved in manipulating atoms.

Nanotechnology is not particularly new. "There's Plenty of Room at the Bottom," by Richard Feynman, discussed the potential for nanoscience in 1959. He argued in support of studying concepts to build equipment needed to work at atomic dimensions.[5] Eric Drexler wrote "Molecular Engineering:

An Approach to the Development of General Capabilities for Molecular Manipulation," in 1981. He built a framework for the study of devices that were able to move molecular objects and position them with atomic precision.[6] A scientist in IBM's Almaden Research Center manipulated individual xenon atoms to form the company's logo on a nickel plate in 1989 (See figure 1).[7] So what's so important about this technology and why should we care about it?

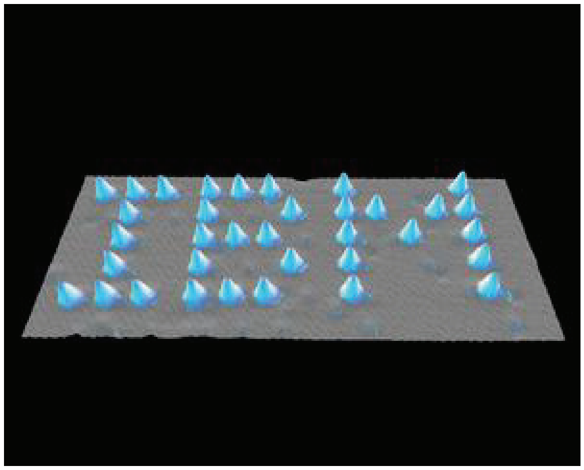

Figure 1: IBM Logo Made of Individual Xenon Atoms (1989)

Overview

The purpose of this report is to describe efforts under way to develop the skills needed to control and manipulate materials at the atomic scale. It will discuss what is driving this research, what applications may result from it, and their implications. The thesis of this paper is that as new fabrication methods are mastered in the quest to continue improving computer processing along the lines of "Moore's Law" out through the 2025 timeframe, these methods will propagate to other applications with the potential to threaten US national security interests. As such, the United States Air Force (USAF) must act to remain aware of advancements in the nanotechnology field.

Chapter 2
Technology Trends

"Self-assembly has the potential for bottom-up fabrication techniques to produce nano- and [microscale]materials and systems, that is, structures and ensembles having spatial dimensions in the range of 1 nm to 1 micrometer—the size of a large molecule to the size of a living cell. Control of the bottom-up products is difficult at present because of the currently limited understanding about how to use these forces. The current state of knowledge about self-assembly and the potential for new products may be comparable to the state of knowledge about the chemical bond at the turn of the previous century. Expanding interest in the fabrication of new materials with these self-assembly methods may give rise to an entirely new discipline."[8]

Shrinking Size

Electronic, mechanical, and optical devices continue to shrink in size. With decreasing feature size, the device cost decreases and its performance increases.[9] This has led silicon microelectronics to transition to the sub-micrometer scale—nano-scale silicon electronics. Many integrated-circuit components in production today consist of devices of nano scale size. These include molecular electronics which utilize individual molecules in their structure.

But as transistors get smaller, more power and heat dissipation issues develop. According to researchers at the Intel Corporation, "the primary challenge in doubling performance is power: reducing leakage (heat) while adding more, smaller transistors (performance) into an even smaller footprint."[10] Additionally, fabrication methods are reaching limits in their ability to continue to shrink components and devices further. This should come as no surprise since much of the technology is over 40 years old. As an example, the technology for semiconductor devices dates back to the 1960s.

2005 marked the 40th anniversary of the invention of the first beam-lead device. In 1965, Lepselter and coworkers at Bell Telephone Laboratories proposed a method of fabricating a semiconductor device structure with an application to high-frequency silicon switching transistors and ultra-high-speed integrated circuits. Their method, called beam-lead technology, consisted of depositing an array of thick contacts on the surface of a slab of planar-oxidized silicon. Excess silicon from under the contacts was removed. This separated individual devices leaving them with beam leads cantilevered beyond the semiconductor. The contacts provided structural support for the device and served as electrical leads. The devices were called beam-lead devices and were used for electronic transistors in integrated circuits.[11]

As Lepselter's beam-lead integrated circuits were being developed at Bell Labs in the 1960s, precision silicon etching technology was developed. In the 1970s, this technology was used for sensor development and garnered the name "micromachining." Other devices were developed including micro-actuators, micro-sensors, and micro-motors. During the 1980s, the term "microelectromechanical structures" (MEMS) was born to describe one of the results of the sensor-actuator field. Beam lead devices became the first example of commercial MEMS.[12]

Today, silicon technology is very mature and reliable. However, as previously mentioned, silicon material, as well as device and circuit technology, is nearing a barrier to further development due to limits in manufacturing methods.

Limits of Silicon Technology

Silicon material and circuit technology has progressed for nearly five decades, but is approaching barriers to further chip development due to limitations of fabrication techniques. The complementary metal oxide semiconductor field effect transistor (CMOS FET) is the basis of current ultra-large-scale integrated circuits and many experts believe that CMOS technology will reach the end of its progression in the 2020 time frame. According to Intel, it will hit physical, technological and economic limits. In the coming decade, Intel's silicon process fabrication technologies will approach the physical limits of atomic structure. At atomic levels, thermal effects will eventually limit how far silicon-based transistors can be scaled.[13]
There are many organizations driving the research to find alternatives to breach the barriers. The Nanoelectronics Research Initiative (NRI) is a consortium of Semiconductor Industry Association (SIA) member companies which seek to accelerate and augment research "beyond CMOS" technologies. The Technology Strategy Committee of the SIA defined its mission as follows: "By 2020 discover and reduce to practice via technology transfer to industry novel non-CMOS devices, technology and new manufacturing paradigms, which will extend the historical cost/function reduction, along with increased performance and density for another several orders of magnitude beyond the limits of CMOS." The SIA's International Technology Roadmap for Semiconductors (ITRS) shows no known solutions in the short term for a variety of technological requirements, including gate dielectric, gate leakage, and junction depth. The 2004 ITRS update represents the seventh international version of the roadmap and reflects input from nearly 1,000 experts and researchers form Europe, Japan, Korea, Taiwan, and the USA. Entirely new device structures and computational paradigms will be required to augment and/or replace standard planar CMOS devices.[14] A few examples

of the alternative technologies being investigated are quantum computing, spintronics, interference devices, bottom-up assembly, and optical switches. These technologies are not without risk and will require dedicated research, however Intel is interested in adopting them if they materialize.[15]

Fiscal Year (all in $M)	**2000 Actual**	**2001 Enact/Actual**	**2002 Enact/Actual**	**2003 Enact/Actual**	**2004 Enact/Actual**	**2005**
National Science Foundation	97	150/150	199/204	221/221	249/254	305
Dept of Defense	70	110/125	180/224	243/322	223/315	276
Dept of Energy	58	93/88	91.1/89	133/134	197/203	211
National Institutes of Health	32	39/39.6	40.8/59	65/78	70/80	89
NASA	5	20/22	35/35	33/36	31/37	35
NIST	8	10/33.4	37.6/77	66/64	62/63	53
EPA	-	-/5.8	5/6	5/5	5/5	5
Homeland Security	-	-/-	2/2	2/1	2/1	1
Dept of Agriculture	-	-/1.5	1.5/0	1/1	10/1	5
Dept of Justice	-	-/1.4	1.4/1	1.4/1	1.4/1	1
TOTAL	**270**	**422/465**	**600/697**	**770/862**	**819/961**	**982**

Table 1: A Summary of Funding Opportunities for Nanotechnology [16]

Chapter 3
Technology Developments

"When fully developed, bottom-up fabrication using self-assembly and related methodologies will be able to produce ordered, precisely controlled nanomaterials and nanodevices not achievable by current methods such as lithography and other top-down techniques."[17]

The Funding Challenge

Semiconductor technology is the foundation of many of the amazing revolutions we are witnessing in computing, communications, consumer electronics, transportation, and health care. This revolution continues as the industry builds successive generations of chips that perform an ever increasing number of functions, run faster, and cost less. The SIA is intent on continuing this revolution and forms consortia like the NRI and other partnerships to fund advanced research and pool resources and ideas. The goal is to maintain technological leadership of US semiconductor companies and keep the innovation engine of the country and the economy vibrant and strong. Continued progress requires a large and coordinated effort in research and development among corporations, governments, and universities.

In the 1990s, federal funding declined in the areas especially critical to the industry's continued success: physical sciences, mathematics, and engineering. This seriously reduced the number of faculty and students in these disciplines, slowing the pace of university research and creating a shortage of skilled workers.[18] According to Microsoft chairman Bill Gates, a shortage of information technology graduates from Western universities is leading companies to call on developing countries to meet research demand.[19] Increasing support for university research has become the SIA's top public policy priority.

Over the past several years, research into nanotechnology has again increased. With this funding, research into new technology areas is underway. The rest of this chapter examines these new areas including: self-assembly, block copolymer directed assembly, electron beam lithography, dielectrophoretic assembly, plasmon-assisted chemical vapor deposition, tailored adhesion, surface-tension self-assembly, peptide-protein self-assembly, and DNA and viral self-assembly.

Nano Self-Assembly

Self-assembly refers to parallel assembly without handling individual particles. A key goal of this technology is to generate structures whose complexity matches that achieved by top-down methods and eventually surpasses it. Nature provides a model of bottom-up assembly as the cell is self-assembled and contains many complex structured components.

One of the most challenging and exciting disciplines of nanoscience is to understand self-assembly methods for forming complex structured components. There have been many successes in constructing individual molecular components such as carbon nanotubes, various molecular electronic devices with components at the 10-100 nanometer range, and manipulating individual molecules by probing devices. However, a key deficiency is the lack of methods for constructing complex devices out of nanometer scale components.[20]

Research today is focused on developing methods to hold, shape, and assemble various molecular components into complex machines and systems. As discussed in the previous chapter, top-down methods for construction of nanostructures have inherent limitations in scale. This is driving researchers to work from the bottom-up. Self-assembly is a bottom-up method of construction where substructures are spontaneously organized into ordered superstructures driven by energy minimization and/or the selective affinity of the substructures.[21]

Recognizing that self-assembly processes and experiments have not been examined by science to the degree that is needed now, Defense Advanced Research Projects Agency (DARPA) and the International Society For Nanonscale Science, Computation and Engineering (ISNSCE) have sponsored annual conferences for the last three years on self-assembly fabrication methods. The 3rd conference was held in Snowbird, Utah on April 23-27, 2006, titled "Foundations of Nanoscience (FNANO06): Self-Assembled Architectures and Devices." The conference methodologies included both experimental and theoretical approaches. The disciplines included chemistry, biochemistry, physics, computer science, mathematics, and various engineering fields including micro-mechanical electrical systems (MEMS). The Conferences on Foundations of Nanoscience have the goal of creating vibrant intellectual community and generating synergism in the area of self-assembly.

As reported in the papers generated by the 3rd Conference on Foundations of Nanoscience and various peer review journal papers published over the last 2-3 years, the actual techniques being studied to assemble particles vary greatly. Different driving forces can be used in the assembly depending upon particle size and particle-surface properties.[22] The research and experimentation efforts toward developing nano fabrication techniques may be loosely divided into two camps: a top-down approach based on lithography, and a bottom-up approach where structures are built one molecule at a time.

The first camp favors methods that can extend the existing planar, deposit-pattern-etch paradigm. Materials are deposited, patterns are transferred, and the patterns are etched to create devices. The limiting step is the pattern transfer. Non-optical methods of lithography are being pursued to overcome this size limitation. "The lithographic process is arguably the key enabling technology for the digital age."[23] Lithography is used to pattern features of complex geometries as small as 50 nm with a remarkable level of perfection and placement (registration) with respect to the underlying substrate enabling hundreds of millions of devices to be fabricated on a single chip. But as the shrinking length scales continue, new imaging materials may be required to meet manufacturing constraints. These methods include block copolymer lithography, electron beam lithography, and nano-imprint lithography.[24]

An entirely new, bottom-up architecture based on nano building blocks such as carbon nanotubes and semiconducting nanowires is being pursued by others. In this approach, nanoscale devices are constructed by direct, three-dimensional synthesis. Transistors are one such example.[25]

The following sections take a look at various methods being explored for self-assembly with brief explanations about the approach and possible applications. A summary table is included at the end of the chapter listing the primary source or user of each method, the convention employed for self-assembly, and current and/or potential applications.

Block Copolymer Directed Assembly

Diblock copolymers are a promising class of materials that self-assemble to form ordered nanostructures. These structures include spheres, cylinders, and lamellae whose shape and dimensions depend on the molecular weight and composition of the polymer. Diblock copolymer lithography refers to the use of these nanostructures in thin films as templates. Thin films of diblock copolymers can self-assemble into ordered periodic structures at the molecular scale of five to 50 nm.[26] They have been used as templates to fabricate quantum dots, nanowires, magnetic storage media, nanopores and silicon capacitors.[27] Blends of block copolymers and corresponding homopolymers self-assemble into ordered phases with controllable shapes and dimensions. They are of tremendous interest for the nanofabrication of sub-30 nm ordered structures, such as photonic crystals, membranes with dense arrays of pores, lithographic templates for patterning applications, and complex, three dimensional structures.[28] They self-assemble to form dense arrays of nanostructures with dimensions and spacing that are difficult or impossible to create by other means or are prohibitively expensive to fabricate using conventional lithographic materials and processes.[29]

Researchers have demonstrated an approach for integrating block copolymers into the lithographic process to enable molecular-level control over the dimensions and shapes of nanoscale patterned resist features while retaining essential process attributes such as pattern perfection, registration, and the ability to create non-regular device-oriented structures.[30] Combining this approach and self-assembling materials with advanced lithographic tools may allow "current manufacturing techniques to be extended to the scale of 10 nm and below to meet the long-term requirements detailed in the International Technology Roadmap for Semiconductors."[31]

Electron Beam Lithography:

Several research groups are conducting electron beam induced surface structuring and three dimensional deposition of nano-materials. The Nanostructuring Research Group at Ecole Polytechnique Federale De Lausanne, Switzerland, is focused on micro and nano structuring of substrates and functional materials. They are investigating focused electron beam induced deposition of materials, patterned laser beam induced deposition of titanium dioxide (titania), and other non classical UV Excimer laser applications and chemical coating processes. Applications of these technologies for the realization/production of functional (electrical, magnetic, wetting, mechanical, and nano optical) properties of materials in research will be realized in the not too distant future.[32]

Electron beam nanolithography on biphenyl and terphenyl based self-assembled monolayers can generate well-defined nanostructures on a variety of substrates including gold, silver, silicon and gallium arsenide. Irradiating these monolayers with electrons induces cross-linking by the expulsion of hydrogen. Cross-linking occurs from the top to the bottom of the monolayer with a "dosage-dependent" gradient.[33] Since the cross-linked monolayers behave as negative resists, an etching procedure can be used to generate three-dimensional structures in the substrate after electron irradiation of the monolayers. Researchers have achieved lateral resolutions of three-dimensional line/space arrays down to 20-40 nm. Single lines have been etched with a minimum width of 11 nm.[34]

The cross-linked monolayers can be removed from the substrate on which they were originally based. The freely suspended nanomaterials are mechanically stable and can bear other materials such as nanoparticles. They have two chemically different surfaces which are suitable for covalent attachment of functional units. Research is ongoing for potential applications of these nanomaterials, for example as ultrasensitive sensor materials.[35]

Dielectrophoretic Assembly

Carbon is a favorite material for researchers producing nanomaterials. Single-walled carbon nanotubes (SWNTs), double-walled nanotubes (DWNTs), bamboo structured nanotubes, nanocoils, and metal-filled nanotubes are examples of these materials. Each can serve as building blocks and provide unique functionalities in novel nano systems.

A problem researchers are facing is that the growth processes for each of these materials are significantly different. This prohibits the direct growth of various nanomaterials onto silicon substrates to build NEMS. Dielectrophoretic assembly of carbon-based nanomaterials is one promising process to overcome this challenge.

Assembly by dielectrophoresis (DEP) is a bottom-up assembly method driven by a combination of AC and DC electric fields. The nanoassembly procedure is fairly straightforward. A 500 nm layer of thermal oxide is deposited on a silicon substrate. Forty-five nanometer thick gold electrodes are created by electron-beam lithography and lift-off on the thermal oxide. A layer of chromium fifteen nm thick is then used to improve the adhesion of the gold electrodes to the oxide. Then the desired carbon-based nanomaterials are suspended and sonicated (disrupted by exposure to high-frequency soundwaves to ensure homogeneity) in ethanol. The chip is immersed in this suspension and a composite AC-DC electric field is applied with a high frequency function generator. After approximately 100 seconds, the nanomaterials are deposited onto the electrodes. The chip is then rinsed in clean ethanol and blown dry with a nitrogen gun.[36]

This method aligns individual nanotubes across microelectrodes,[37] and can also be used to assemble individual nanotube arrays across nanosized electrodes. The performance of these devices has been investigated as lateral emitters with potential use in vacuum sensing applications.

This bottom-up assembly method can be used with other conventional top-down silicon micro and nano machining techniques. By using different nanomaterials assembled by an identical process, complex nanoscale systems and devices can be produced. Different nanomaterials will provide different functionality.

Plasmon Assisted Chemical Vapor Deposition (CVD)

CVD is a fabrication technique used by both camps—top-down and bottom-up. For top-down thin films, it is regarded as one of the most effective means of high-throughput, high quality deposition. For the bottom-up approach, CVD is used to synthesize silicon nanowires and single-walled carbon nanotubes.[38]

CVD requires heat. Typically, the entire process takes place inside an oven. However, if the heat is localized, so is the deposition. Localized heating with lasers (laser assisted CVD) has been used to fabricate high aspect ratio structures such as dots, lines, and rods at the microscale level of detail. This fabrication method uses a laser beam focused on the sample to locally heat the substrate in a CVD environment. The size of the deposition is limited to the diffraction-limited spot size of the laser, which is on the order of 1 micron.

Over the past decade, a systematic study (both theoretical and experimental) of photon-electron interactions in nanoscale structures has developed a number of useful technologies. While the physics underlying these interactions is complex, the basic principle involves the resonant phenomena at these length scales. "Noble metal nanoparticles have absorption resonances in the visible range of the electromagnetic spectrum related to collective electron excitations known as surface plasmons."[39] The heat transfer of the nanoparticles are predicted to be greatly reduced when the particle size approaches the phonon mean free path of the substrate material. Deposition at the nanoscale can be accomplished by employing these effects. This is the principle behind Plasmon Assisted CVD.

Plasmon Assisted CVD focuses a low-powered laser beam onto a substrate coated with gold nanoparticles. The wavelength of the laser beam is selected based upon the natural resonance in the gold particles. When the laser beam strikes the gold particles, energy from the laser is transferred to the particles and they heat up several hundred degrees. The hot gold particles decompose nearby gas molecules forming microscopic deposits on the gold nanoparticles. Researchers using this process have developed wires a few tens of nanometers in diameter of lead oxide on a glass substrate. The hope is that this technique may enable microdevices to be constructed at even smaller scales in the future.[40]

Tailored Adhesion

Tailored adhesion is a passive approach to handling self-assembled particles in parallel. To date, researchers have demonstrated the ability to transfer ordered assemblies of particles with diameters ranging between 100 micrometers and 60 nanometers from one surface to another. This process allows these particles to be ordered by self-assembly techniques. Subsequently, they can be integrated into standard surfaces without specific patterning. Adhesive forces are precisely tailored. They are strong enough to hold the ordered particles after assembly, yet are weak enough to release these particles onto a target substrate when brought into close contact. In this way, the assembly process is carried out on a specialized template.

In building complex structures, particles are first assembled at a low level of adhesion. They are then transferred onto a carrier. Finally, they are integrated onto the substrate at the highest level of adhesion. This concept is called "adhesion cascade."

Surface Tension Self Assembly:

Fluid surface tension forces provide another method for self-assembly. Surface tension was applied to the self-assembly of three-dimensional microstructures by out-of-plane rotation of flat parts as early as 1993. Surface tension self-assembly fabrication relies upon minimization of the energy of the free liquid surface by achieving an equilibrium configuration.[41]

Due to the high surface area-to-volume ratio, surface tension is a dominant force at the micro- and nanoscale. Researchers have a developed a class of biomimetic micro-actuators powered by the surface tension of water. This class of actuators was inspired by the hygroscopic spore dispersal mechanism of ferns. The first nanoactuators had 80 nm feature sizes and 800 nm total device size.[42]

Peptide-Protein Self-Assembly:

Mother Nature provides many fundamental building blocks in biology and lessons on macromolecular materials constructs with enormous variety of functionalities for a wide range of practical applications. Peptides and proteins are some of the most useful groups of molecules because of their immense information content. Polypetides, depending upon their amino acids and sequences, have specific molecular conformations that determine the molecule's specific recognition properties. The sequence dictates the self-assembly characteristics of the polypeptide and its structure / molecular recognition.[43]

Researchers have adapted molecular biology approaches and developed protocols for genetically engineered polypeptides that can be used for a wide range of materials and medical-related applications. Researchers at the Self Organising Molecular Systems (SOMS) Centre, University of Leeds Centre for Nanotechnology, United Kingdom, have employed biological properties to design simple peptides that self-assemble in one-dimension in a hierarchical manner to form a variety of well-defined twisted elongated nanostructures such as tapes (single molecule in thickness), ribbons (a pair of stacked tapes back to back), fibrils (a bundle of stacked ribbons) and fibres (a pair of fibrils interacting edge-to-edge). Designed fibrils have been used as templates for the guided polymerisation of silica and the formation of hollow chiral silica nanotubes for use in catalysis and chiral separation. Peptide gels have been self-assembled *in situ* in teeth cavity-like lesions. They increase enamel remineralisation which can lead to tooth repair. This property has been ascribed partly to the ability of the peptide fibrils to template hydroxyapatite crystals mimicking the natural process of biomineralisation, and may have wider implications for usage of self-assembling materials in bone tissue engineering.[44]

DNA

Nucleic acids (DNA and RNA) contain unique structural properties that make them attractive materials for engineering nanoscale structures and devices. DNA serves as the primary genetic storage medium for life. RNA serves in biological storage, regulation, catalysis, and synthesis. Synthetic nucleic acid systems can be designed to self-assemble into complex structures by appropriately arranging the sequence of bases in each strand. Nucleic acid nanotechnology is a field devoted to developing capabilities for applications in molecular robotics, fabrication, computation, biosensing, electronics, and medicine.[45]

Many research groups are developing nanofabrication methods based on DNA self-assembly. Biological morphogenesis, where a genome programs a cell to self-assemble an organism, provides one example of how complex nanoscale devices can be fabricated.[46] DNA nanostructures do not have useful electronic properties themselves, however their value lies in their utility as scaffolds for organizing and positioning functional materials with nanometer scale precision. One of the challenges of DNA based structures has been the lack of control of the final lattice size because terminating events are not programmed into the self-assembly. Still, the methods hold enormous potential for designing molecular printboards whose complexity can rival those produced by lithographic methods.[47]

Researchers at Arizona State University have demonstrated the design and construction of fully addressable DNA tile nano grids with each location bearing a unique biochemical label. They have used self-assembled DNA nano grids to direct the self-assembly of five nanometer gold nanoparticles into periodic nanoarrays with accurate control of inter-particle spacing. ASU researchers have demonstrated a novel and cost-effective strategy to produce finite size DNA nanostructures containing four, eight, and twelve helices and used them to investigate the mechanism of DNA tube formation. This control is crucial for future nanoelectronic devices assembled on a DNA based molecular printboard.[48]

Angela Belcher, *Scientific American's* "Research Leader of the Year," has the goal "to have a DNA sequence that can code for the synthesis of any useful material."[49] She worked with the DNA sequence of the M13 bacteriophage, engineering a version that latched onto quantum dots. Her work focuses on custom-evolved viruses that synthesize nano-scale wires and arrays.

Viral Self Assembly

Viruses pose yet another approach to manipulation of nanoscale particles with a range of applications from materials to medicine. The inherent properties of viruses are used as synthetic templates. Although viruses are normally thought of as disease causing agents, they can be chemically and genetically modified to be highly useful as molecular assemblers. "In particular, the chemically plastic interior interface of virus architectures (and other protein cages) has been used to direct the nucleation and growth of hard inorganic materials."[50]

Using viruses as nanoscale scaffolds for devices offers control over positioning nanoscale components on the protein scaffold, enabling bottom-up self-assembly of nanoscale devices. "Using Cowpea Mosaic Virus, modified to express cysteine residues on the capsid exterior, gold nanoparticles were attached to the viral scaffold to create a three dimensional pattern with specific interparticle distances."[51] The gold nanoparticles were interconnected using molecular wires and switches. The three dimensional spherical conductive network which resulted from this method is only 30 nm in diameter. It can switch between two conduction states like a transistor based on the applied voltage.

Biology and the manipulation of viruses may be the key to producing light-weight, inexpensive, and high-performance batteries. Potential applications include transforming military uniforms into power sources and improving electric and hybrid vehicles. MIT researchers, like Angela Belcher, have engineered viruses to assemble battery components that can store three times as much energy as traditional materials. This is accomplished by packing highly ordered materials into very small spaces.[52] The battery looks like a thin sheet of cellophane. Researchers from MIT have genetically modified other viruses to interact with solutions of inorganic semiconductors producing self-assembling metal films and wires with diameters of only a couple nanometers.[53]

Summary

An interesting aspect of this research is the multitude of approaches being pursued and the worldwide aspect of this work. Steady progress is being made in each approach. There are no clear signs that any one approach will far exceed the others. This is beneficial for finding a viable solution, however it makes it difficult from a national defense perspective, as it makes it impossible to predict where institutions like DARPA and AFRL focus their research dollars.

The following table summarizes the self-assembly methods examined in this chapter. It lists the primary sources and users, the convention employed to achieve self-assembly, and possible applications.

METHOD	SOURCE/USER	CONVENTION	APPLICATIONS
3.2 Block Copolymer Directed Assembly	University of Wisconsin-Madison & Lab for Micro and Nanotechnology, Switzerland	Uses thin film templates at the 5 to 50 nm scale	Quantum dots, nanowires, magnetic storage media, nanopores and silicon capacitors
3.3 Electron Beam Lithography	Ecole Polytechnique Federale De Lausanne, Switzerland, University of Heidelberg, Germany; Inst. for Molecular Biophysics, Maine; University of Bielefeld, Germany; Chinese Academy of Sciences, China	Uses irradiation of monolayers with electrons	Potential application for ultrasensitive sensor materials
3.4 Dielectrophoretic Assembly	Inst of Robotics and Intelligent Systems, Switzerland; Zhejiang University, China	Uses Composite AC-DC electric field	Lateral emitters with potential use in vacuum sensing applications
3.5 Plasmon Assisted Chemical Vapor Deposition	Caltech, Stanford University, and NYU	Uses low-power laser beam	Si nanowires and single-walled carbon nanotubes
3.6 Tailored Adhesion	IBM Research, Zurich Research Lab, Switzerland	Uses forces inherent from large surface-to-volume ratio	60 nm gold nanocrystals
3.7 Surface Tension Self-Assembly	University of Michigan	Uses forces inherent from large surface-to-volume ratio	Scalable biomimetic actuators
3.8 Peptide-Protein Self-Assembly	University of Washington, Seattle; New York University, NY, University of Leeds Centre for Nanotechnology, United Kingdom	Uses amino acid sequences	Materials and medical related applications
3.9 DNA Self-Assembly	Arizona State Univ; California Inst. Of Technology	Uses DNA as "scaffolding"	Molecular print boards
3.10 Viral Self-Assembly	MIT	Uses viruses as "scaffolding"	Nanowires, Batteries

Table 2: A Summary of Self-Assembly Methods

Chapter 4

Applications and Implications

"Rather than making machines that mimic animals, Angela Belcher is coaxing living creatures to produce machines," Popular Science wrote. A "pioneer in this field, [she] has engineered viruses that can grow semiconductor materials, microscopic biosensors and liquid-crystal structures for computer screens or DNA-storage devices. It takes her just three weeks to 'evolve' a virus to produce a new substance on its surface."[54]

"Any sufficiently advanced technology is indistinguishable from magic."[55]

Implications of Self-Assembly

As researchers develop skills and techniques to manipulate substances at the nanometer level and produce complex devices, new applications will emerge. Potential applications include information technology, health care, environmental protection, energy, and genetic engineering, many of which can have military or defense ramifications. A specific example is recording media. A nanoscale memory array could improve memory densities of devices such as magnetic drives and tapes, optical disks, holographic media, magnetic random-access memory (RAM), by more than an order of magnitude.[56] Organizations involved in this research include IBM, Intel, Interuniversity Microelectronics Center, HP, Motorola, LETI, STMicroelectronics, Microelectronics Technology Laboratory, the French National Center for Scientific Research, Nanotube Manufacturers, Nanosys, Carbon Nanotechnologies, Helix Materials Solutions, and Nanodynamics.

Information Technology: Nanotechnology advancements in electronics will lead to better capabilities. Carbon nanotubes can be used in electronic components and displays making displays better and more flexible, enabling higher resolution filming, and improving drive storage. These, in turn, may lead to printable large-area displays, wearable electronics, paper-like electronic newspapers, low-cost photovoltaic cells, and ubiquitous integrated sensors and radio-frequency identification tags. In the far-term, applications include quantum computing, morphing capabilities, self-repair, and advancements in biotechnology.

Health Care: Given Imaging is redefining gastrointestinal diagnosis by developing, producing, and marketing innovative, patient-friendly products for detecting gastrointestinal disorders. This version of new imaging technology is currently marketed in the US and over 60 other countries. It has benefited more than 400,000 patients worldwide.

Researchers are also exploring ways to use implantable biomedical nanotubes as artificial nerve cells to control severe pain and move otherwise paralyzed muscles. Writing in *Advanced Materials*, Nicholas Kotov of the University of Michigan, and colleagues describe how they have used carbon nanotubes to connect an integrated circuit to nerve cells. The new technology offers the possibility of building an interface between biology and electronics to improve life.[57]

Yet, there are some technologies that can advance health care that could be made to serve more sinister purposes. Devices that can explore the digestive system could be made to cause as well as diagnose illnesses. Neural interfaces that can eliminate pain could also b e made as to cause it, potentially raising the art of torture to a whole new dimension.

Even more amazing is synthetic biology—Synbio. Dubbed "genetic engineering on steroids," it results from the convergence of nanoscale biology, computing, and engineering. Using a laptop computer, published gene sequence information, and mail-order synthetic DNA, the sophistication level required to construct genes or entire genomes from scratch (including those of lethal pathogens) is not far beyond the level of some advanced high school labs.[58] These genomes offer the potential to cure disease. Yet, in the wrong hands, they could cause it.

"Eckard Wimmer knows of a shortcut terrorists could someday use to get their hands on the lethal viruses that cause Ebola and smallpox. He knows it exceptionally well, because he discovered it himself."[59] Wimmer built a live, fully artificial virus in the lab from scratch. "It was a variation of the bug that causes polio, yet different from any virus known to nature."[60] The virus was made in his small laboratory at the State University of New York on Long Island with equipment and chemicals on hand, genetic code picked up for free on the Internet, and hundreds of tiny bits of viral DNA purchased on line.

The Current State of the Science

M.C. Roco, the Senior Advisor to the National Science Foundation and the U.S. National Science and Technology Council's Subcommittee on Nanoscale Science, Engineering and Technology has identified four generations for nanotechnology products: passive nanostructures, active nanostructures, systems of nanosystems, and molecular nanosystems. The worldwide focus 2001-2005 was on basic discoveries and production of passive nanostructures, such as nanotubes, nanolayers, and nanosized particles. In 2005, the transition was toward active nanostructures and nanosystems. Examples of active nanostructures are: nanoelectromechanical systems, nanobiodevices, targeted drugs and chemicals, light-driven molecular motors, nanoscale fluids, plasmonics, laser-emitting devices, adaptive nanostructures, and energy storage devices.[61]

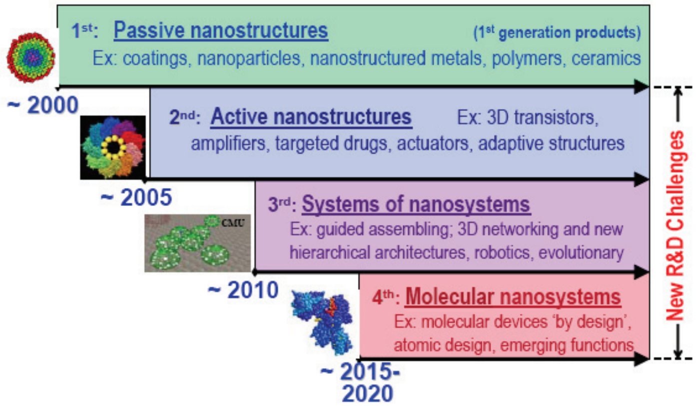

Figure 2: Timeline for Nanotechnology Prototyping and Commercialization[62]

In 2000, the NSF estimated $1 trillion worth of products will incorporate nanotechnology in key functional components worldwide by the year 2015 and would require about 2 million workers in nanotechnology and about three times as many jobs in supporting activities. These estimates were based on an industry survey in the Americas, Europe, Asia and Australia. The estimates continued to hold in 2005 as forecasts made by Mitsubishi Research Institute (Japan), Deutche Bank (Germany), Lux Research (U.S.) and other organizations support the estimated $1 trillion by 2015.[63]

Federal agencies in the U.S., Europe, and Japan began to pursue programs into the various branches of nanotechnology in the 1990's. Various initiatives developed such as the National Nanotechnology Initiative in the U.S., to push forward nanotechnology as a key interdisciplinary technology. Today, nanotechnology is established as a specific field of research and development in nearly all industrialized countries. The worldwide investment in nanotechnology research and development (R&D) reported by national government organizations and the European Community has increased from $432 million in 1997 to about $4.1 billion in 2005. Today, nanotechnology research represents twenty percent of the education research and development budgets fro Korea and Taiwan, and 65 percent for the United States. In the industrial sector, these percentages are reversed, with only five percent of U.S. industrial research and development and 60 percent of Korean and Taiwan commercial research and development is spent on nanotechnology. Across the major developing countries, national research spending is rather similar, with 20-25 percent of the state-funded research and development being spent on nanotechnology.[64]

Currently, the U.S. and Japan are the leaders in nanotechnologies R&D at the global level, with some sources putting the U.S. first[65], and others ranking Japan first.[66] U.S. investment accounts for more than one-third of global spending with annual public and private investment of $3 billion. The U.S. also ranks first in the number of business start-ups, publications and patents. Annual spending in Japan in 2003 accounted for about 630 million Euros, with 460 million Euros provided by the Ministry of Education provided and the bulk of the remainder by the Ministry for the Economy, Trade and Industry.

In China, rapid development of China's nanotechnology industry in the past five to ten years is due in large part to the intervention of the central government. Nanotechnology has garnered state funding through a national research and development plan providing investment for projects mainly in the field of nanomaterials. On-going projects include mass production of nano-diamond coating materials, carbon nanotubes and nanowires, sensor network systems for security monitoring, nanomaterials for energy-saving, self-cleaning, chemical and bio sensor systems and network for environment monitoring and disease diagnosis. China has an internal market for nanotechnology products and systems estimated at more than 4.5 billion Euros. Although the industry in China is still in an early stage with considerable challenges in the field of research commercialization, infrastructure, and human resources, it is set to grow to more than 120 billion Euros by 2015.[67]

Potential Future Scenarios

To best understand the impacts these technologies may have, it is useful to explore potential alternative nanotechnology development scenarios. One non-governmental organization, the Millennium Project has done this as it seeks to provide early warning and analysis of global long-range issues, opportunities, and strategies. In its report titled "Future Science and Technology (S&T) Management Policy Issues – 2025 Global Scenarios by Jerome C. Glenn and Theodore J. Gordon identified four possible scenarios in which nanotechnology plays a significant role:[68]

Scenario 1. S&T Develops a Mind of its Own: "The rate of scientific discoveries and advanced technological applications exploded. A global science/social feedback system was at work: science made people smarter, and smarter people made better and faster science. Better and faster science opened new doors to discovery, and new doors led to synergies and solving of old roadblocks. Removing the roadblocks created new science that made people smarter. S&T moved so fast that government and international regulations were left in the dust. Science and technology appeared to be taking on a mind of its own."[69]

This scenario is the least benign and evidence that we are following this path is readily available. As this report has shown, research efforts strive to continue Moore's Law. As Moore's Law continues, it not only accelerates computer capacity, but all phenomena associated with computers. As such, technology can take on "a mind of its own."

Scenario 2. The World Wakes Up: "The murder of 25 million people in 2021 by a self-proclaimed Agent of God who created the genetically modified Congo virus finally woke the world up to the realization that an individual acting alone could create and use a weapon of mass destruction. This phenomenon became known as SIMAD—Single Individual Massively Destructive. Regulatory agencies and mechanisms were put into place to control the science- and technology-related dangers that became apparent. Education was a big part of the answer, but connecting the educational systems with the security systems was disturbing to some people. Nevertheless, further individual acts of mass destruction were prevented. International and government regulations did manage the S&T enterprise for the public good."[70]

The technology to empower an individual to create a virus such as this is being developed now. Oversight is currently provided by volunteer boards known as institutional biosafety committees. The National Institutes of Health set guidelines on federally funded schools and private labs to appoint such boards. A National Academy of Sciences report recommended the committees take on a larger role in policing research that could lead to more powerful biological weapons in 2004, but many of these boards appear to exist only on paper and are not providing sufficient oversight.[71] It is hard to imagine how effective regulatory steps could be put in place even after a catastrophe such as described in scenario 2 takes place, as the knowledge and ability to manipulate genes and manufacture viruses is becoming ubiquitous.

Scenario 3. Please Turn off the Spigot: "Science was attacked as pompous and self-aggrandizing, as encouraging excesses in consumption, raising false hopes and—worse—unexpected consequences that could destroy us all. Particularly worrisome was accidentally or intentionally released genetically modified organisms and the potential for weapons of mass destruction. The poor were ignored. A science guru arose to galvanize the public. A global commission was established but failed because of corruption. But a new commission with built-in safeguards seemed to be working."[72]

This scenario also involves a catastrophe--a bioterrorist "Pearl Harbor. But it also requires an individual to come forward to "galvanize" the public.

A key set of questions in this scenario is who would this leader be, and where would (s)he come from?

Scenario 4. Backlash: "Control was low and science moved fast, but negative consequences caused public alarm. The golden age of science was hyped by the media, but it all proved to be a chimera. Some of the most valued discoveries and new capabilities had a downside and surprises abounded. Rogue nations took advantage of some of these shortcomings. The level of concern rose. Mobs protested. Regulation failed. Progress stalled. And corporate (or government) scientists frequently felt pressure from within their organizations. Both corporate and government organizations could not be counted on to self-regulate. What's next?"[73]

In this last scenario, control remains low and science continues to move fast. The challenge here is "to regulate on a global scale would require regulators more insightful than the scientists doing the research."[74] This is not a situation likely to occur. Outlawing research is not practical either, as the research efforts would merely migrate elsewhere, or simply move underground.

All four scenarios present serious future challenges. Chapter 5 attempts to address how these challenges are best met.

Chapter 5
Recommendations and Conclusion

"It would be possible – fully legal – for a person to produce full-length 1918 influenza virus or Ebola virus genomes, along with kits containing detailed procedures and all other materials for reconstitution," said Richard H. Ebright, a biochemist and professor at Rutgers University. "It is also possible to advertise and to sell the product, in the United States and overseas." [75]

"There are two ways of dealing with dangerous technologies…One is to keep the technology secret. The other one is to do it faster and better than everyone else. My view is that we have absolutely no choice but to do the latter."
Tom Knight, *New Scientist*, 18 May 2006

Recommendations

Top-down nano-technology fabrication is prevalent today. The real breakthrough will come with bottom-up self-assembly fabrication. As shown in chapter 3 and summarized in table 3, there are many differing approaches to self-assembly and it is very difficult to determine which holds the most promise. Currently, there is no dominant method, nor is there a reliable way to predict which method or methods will work best in the future.[76]

The following recommendations are designed to position the Air Force to take advantage of the advances in this field and prepare for the potential threats:

(1) The Air Force, through Air Force Research Lab (AFRL), Air Force Institute of Technology (AFIT), and Air Force Office of Scientific Research (AFOSR), should ensure that their respective scientific communities stay engaged in basic research in nanotechnology broadly defined. Specifically, they should track progress being made in self-assembly techniques through "Foundations of Nanoscience, Self-Assembled Architectures and Devices" and other conferences and research efforts worldwide.

(2) Groups such as the National Air and Space Intelligence Center (NASIC) should monitor closely the scientific programs in nanotechnology, particularly in other countries.

(3) Air Force Material Command (AFMC) should be tasked to catalog and monitor commercial applications in nanotechnology, specifically focusing on civilian designed, commercially available nanoelectronics and nanostructures.

(4) Information from the above efforts should be reviewed annually by AFRL in conference or symposium including civilian academics to gauge

progress made in nanotechnology and its linkages to synthetic biology, biotechnology, and progress toward self-assembly.

(5) The ETC Group (action group on erosion, technology and concentration), an international civil society organization based in Canada dedicated to the conservation and sustainable advancement of cultural and ecological diversity and human rights, has made a recommendation concerning Synbio—"to facilitate coordinated global action, an international body should be established to monitor and assess societal impacts of emerging technologies, including synthetic biology."[77] Self-assembly is another one of those emerging technologies that fits into this group. The rationale for this can be found in Tom Knight's quote above. Self-assembly technology is not being kept secret and it is not something we can do faster or better than anyone else. This should cause us great concern. It is advancing the state of the art in nanoscience and will have impact on biotechnology, computing, and engineering.

Conclusion

This paper began by looking at a trend. The trend is the continuous shrinking of electronic transistors over the last 30-40 years in order to continue Moore's Law. By tracking this trend, barriers to continued shrinking of devices have been discovered. This led to the exploration of various nano and nano-scale technologies, including methods of self-assembly to overcome these barriers. Industry is intent on finding ways to overcome these barriers in order to continue to increase the performance of integrated circuits and decrease computing cost.

Yet, interest in miniaturization is not unique to the semiconductor industry. There are many applications where smaller is better. Nano-enabled systems incorporate functional complexity directly into each individual nanoparticle. The ability to build from the bottom-up and take advantage of the unique quantum properties of materials at the nanoscale holds rewards for far more than just the semiconductor industry. That is the entire premise of this study.

Diffusion to other areas is the wildcard in the 2025 timeframe. Transistors today are at the diffusion stage. They not only dominate the application area in which they were initially adopted, but they have been adopted for purposes to which the earlier device was never applied. The transistor replaced the vacuum tube for conventional electronics and now appears in applications which vacuum tubes were never used, such as automobile ignitions and automatic exposure controls in cameras.[78]

The impact of nanotechnology will reach beyond next-generation integrated circuits. Nanoelectronics is being driven by industry seeking hard disks with larger capacity, new forms of nonvolatile memory, smaller and more flexible displays; stronger batteries and power sources; more efficient networks; quantum computing; and more. Unfortunately, the technology can also be employed to threaten, harm, and/or kill. It has the potential to cross into other disciplines and an early warning / early listening system is required to prevent the catastrophes identified in the 2025 scenarios or other "Pearl Harbor" type attacks.

There is no doubt that the countries, corporations, and even individuals that achieve breakthroughs in nanotechnology and bottom-up self-assembly will revolutionize many products, processes, and capabilities. Unlike major technological breakthroughs of the past, such as the industrial revolution and nuclear power, this is an area in which individuals will be able to participate. The synthesis of biological and mechanical systems will propel us into a whole new world.

We do not know where the science and technology will take us with any specificity. But it is safe to say achieving bottom-up self-assembly would be truly revolutionary. Not knowing and participating in the progress toward that goal would be a serious dereliction of duty in defending the United States.

Appendix

Summary of Potential Future Nanotechnologies

Device	Possible Applications	Advantages	Disadvantages	Remarks
Single-electron transistors (SET)	Logic element	Small size Low power	1. Sensitive to background charge instability. 2. High resistance and low drive current. 3. Cannot drive large capacitive (wiring) loads. 4. Requires geometries <<10 nm for room-temperature operation.	Use of Coulomb blockade in nanocrystal "floating-gate"- type nonvolatile memory demonstrated. May improve retention time.
Quantum dot (quantum cellular automata, QCA)	Logic element	Small size	1. Multiple levels of interconnection across long distance difficult. 2. Room-temperature operation difficult. 3. New computation algorithms required. 4. Method of setting the initial state of the system not available. 5. Single defect in line of dots will stop propagation.	Devices demonstrated at low temperatures. QCA architectures extensively investigated.
Resonant tunneling diode (RTD)	Logic element Dynamic memory	Small size	1. Tunneling process sensitive to small film thickness (tunneling distance) variation, leading to process control difficulties. 2. Requires dc bias, large standby power consumption 3. Multivalue logic sensitive to noise margin 4. Speed of RTD circuits likely to be determined by the conventional devices required in the circuit.	Small- to medium-scale circuits demonstrated. Most demonstrations on III–V compound semiconductors.
Rapid single-flux quantum (RSFQ) device	Logic element	Very high speed possible	1. Requires liquid helium temperature. 2. Lacks a high-density random-access memory. 3. Requires tight process tolerance.	Very-high-speed (THz) circuits demonstrated.
Two-terminal molecular devices	Logic element Memory	Small size	1. No inherent device gain. 2. Scaling to large memory size may be difficult without gain. 3. Placement of molecules in a circuit difficult and not yet demonstrated. 4. Temperature stability of organic molecules may be	Sixteen-bit cross-point memory demonstrated.

			problematic.	
Carbon nanotube FET	Logic element	Ballistic transport (high speed) Small size	1. Placement of nanotubes in a circuit difficult and not yet demonstrated. 2. Control of electrical properties of carbon nanotube (size, chirality) difficult and not yet achieved.	Device scaling properties not yet explored. Inverter circuit demonstrated.
DNA computing	Logic element	High parallelism	1. Imperfect yield. 2. General-purpose computing not possible.	

Figure 3: Summary of Possible Future Devices and their Salient Attributes [79]

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The Center focuses on education, research, and publications that support the integration of technology into national strategy and policy. Its charter is to support faculty and student research, publish research through books, articles, and occasional papers, fund a regular program of guest speakers, host conferences and symposia on these issues, and engage in collaborative research with U.S. and international academic institutions. As an outside funded activity, the Center enjoys the support of institutions in the strategic, scientific, and technological worlds.

An essential part of this program is to establish relationships with organizations in the Air Force as well as other Department of Defense agencies, and identify potential topics for research projects. Research conducted under the auspices of the Center is published as Occasional Papers and disseminated to senior military and political officials, think tanks, educational institutions, and other interested parties. Through these publications, the Center hopes to promote the integration of technology and strategy in support of U.S. national security objectives.

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