

Nanotechnology, a stimulus for innovation

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The virtues of nanotechnology have combined to make the subject worthy of special emphasis in the research community and a source of new commercial products. This has been the result of a synergistic combination of major historical technological advances, recent scientific discoveries (especially of new scientific principles), and a futuristic vision that supports widely acclaimed goals. Surprisingly complex self-assembled structures (new materials) resulting from nature's forces have been discovered and are under intense examination for exploitation. The forces lead to biological complexity, also a result of self-assembly, and are beginning to be understood. The subject has opened new scientific frontiers and has begun to redirect scientific pursuit from somewhat narrow fields of inquiry within scientific disciplines to include broader objectives related to technologies and useful materials. Aspects of the subject that make it particularly attractive for high-level support are examined. Nanotechnology as it impacts fields of electronics and information, biology, chemistry and medicine, energy, the environment, transportation, and especially that of materials, is briefly considered.

THE worldwide thrust in nanoscience and nanotechnology represents a relatively new phenomenon in which the scientific community has gained strong administrative and political support at high levels for research at fundamental levels in a number of scientific and engineering disciplines. Differences in this thrust relative to the normal course of evolution in discoveries and inventions are discussed herein, along with the reasons why this approach has gained support at such high international levels. Historical track records, the potential for innovation, and the impact of potential gains from this research are important ingredients characterizing the thrust. This has set the foundation for the current successful initiative in this interdisciplinary scientific endeavour.

Stimulus for nanotechnology as an area of emphasis

Convergence of various events led to the recognition of nanotechnology as an area for special emphasis. These included a recognition of new phenomena that would be necessary to extend the progress associated with the gen-

eral area of information technology, scientific discoveries of new instruments and materials, and an awareness of an information frontier that offered a rich supply of new principles, phenomena, materials, and opportunities to enrich societal functions. The elements stimulating this area for emphasis are outlined in Table 1.

The research disciplines in academia often focus on questions appreciated by peer groups, leading to greater depth within the disciplines. However, depth within a given discipline does not represent the only path to discovery of major importance. In fact, with the evolving strength of disciplines, the fertile frontier of discovery requiring knowledge across discipline boundaries had been somewhat neglected for decades.

This is where the concept and thrust in nanotechnology represents a substantial difference to the manner in which knowledge and technological innovation is pursued. Frontiers of knowledge involving new concepts across the standard discipline lines represent relatively unexplored sources for innovative discovery. The atom and the molecule have been the source of specialized disciplines in physics, chemistry, materials and medicine. Semiconductor behaviour has provided the electronics engineer with remarkably productive developments. However, the behaviour of matter with dimensions larger than a molecule, but smaller than the feature sizes in today's semiconductor devices, represents a frontier not explored by these disciplines due to its complexity. Heretofore, tools were lacking that had the capability to characterize the materials and to evaluate performance. Once the tools became available for understanding the nature of nanometer-sized bits of matter, all of these disciplines have found a rich source of new phenomena to nourish innovation and new products.

While searching for new and innovative approaches to science and technology, it is necessary to recognize that the goals and ultimate utility of nanotechnology are not different from those that have led innovation for decades. The principal drivers for innovation in society, in general, include improved food, clothing, shelter, safety, transportation, communication, energy (production, storage and transformation), information (discovery and transmission), health and medicine. These elements are the basis for improvement in human welfare, and have been the driving force for innovation with past technological revolutions. It is unlikely that new basic human needs will emerge from scientific discovery, but the relative effort given to the fundamental objectives may shift

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Table 1. The stimulus in areas related to nanotechnology

Event(s)	Description
Rapid technological progress	Moore's Law and the exponential progress of enhanced microelectronics (size reduction, speed enhancement, increased capacity) for decades has produced a true revolution in technology, with a major positive impact for society.
Recognition of future technological challenge	The continued miniaturization of semiconductor devices will meet a technological barrier within the next 10–15 years without new principles, materials, and phenomena to continue the trend.
Emergence of new instrumentation	The scanning tunneling microscope, plus many related derivative instruments (e.g. scanning force microscope) paved the way for new discoveries.
Discovery of new scientific principles	Quantized conductance surprised researchers when the phenomenon was discovered. Nanometer-dimensioned electronic devices demonstrated quantum interference, indicating the new principles required for design and performance at these dimensions. First principle physics-based computational methods coupled with massively parallel computing capabilities to predict materials properties in small dimensions, and to fabricate materials by design.
Paths for fabrication of new materials	Buckminsterfullerene (C ₆₀) discovered; carbon nanotubes follow, with surprisingly desirable properties. Life processes have produced materials that have intrigued researchers with products having highly desirable properties (e.g. spider silk, shells of crustaceans). Supramolecular complexes are recognized as the first step toward self-assembled materials; great variety, new principles to be discovered; a beginning to understanding life processes.
New scientific frontiers for a wide variety of technological opportunities	The future functions of information storage, retrieval, and manipulation appear to have significant increases in performance with scientific discovery. New materials for a variety of purposes should follow scientific principles of self-assembly. Biological/medical advances continue at a rapid pace, stimulated further with new tools and scientific principles from the physical sciences. Impact of new materials for environmental improvement, energy storage and efficiency, transportation, etc. appear attractive.
Anticipated economic impact	The combined worldwide economic impact of new materials, electronics, pharmaceuticals and health care, and chemical and aerospace manufacturing is projected to be approximately one trillion dollars within the next 15–20 years.

as a result of opportunities perceived from the discovery of new knowledge. As an example, a century ago agriculture consisted of 23% of the total labour in the United States, and medicine consisted of a few percent. Today, agriculture consists of about 3% of gross domestic product (GDP), and health/medicine is about 14% of GDP. The consequences of tomorrow's nanotechnology innovations are likely to bring new opportunities within the broad spectrum of societal enterprises. Nanotechnology aspires to these goals, and is demonstrating significant progress toward achieving success with these efforts.

Stating scientific goals in terms of fundamental societal impact is contrasted with goals set by peers in an academic discipline, where in-depth pursuits lead researchers to communicate with highly specialised terms understood within a peer group. Broadening of the perspective in setting these goals is a consequence of the many opportunities that have arisen from examining a state of matter heretofore considered inaccessible (that at nanometer dimensions), and which has become of interest due to the availability of new tools and more powerful models by which to predict behaviour. An excellent overview of the subject of nanotechnology appears in the September 2001

issue of *Scientific American*¹. The breadth of anticipated opportunities illustrates the cross-disciplinary nature of the goals that are stimulating today's research agenda.

As mentioned above, initial visions involving nanotechnology emerged as 'smart, self-replicating robots'. Little constructive research was published with such far-reaching but remote goals. Today's goals for nanotechnology are gaining credibility within the scientific community², and are significantly modified from those initial visions based on imagination with relatively little experimental basis or sound theory.

Stimulus from historical progress

The revolutionary advances giving rise to the semiconductor and computer revolution in the information sciences represents one of the most outstanding technological developments of the modern age. When the performance of any system increases by a factor of two, the results are usually profound. The performance of computers, with continued miniaturization through improved processing and materials, however, has increased by a factor of two

every two years for the last four decades! The continuation of this trend was not predictable in the 1960s. The semiconductor industry illustrates a remarkable example of a revolution in progress. Moore's Law³ continues with extensive collaboration and planning, documented by the International Technology Roadmap for Semiconductors (ITRS)⁴. Projections for these semiconductor devices suggest that in 15 years the feature sizes will approach roughly 10 nanometers. Limits to the further miniaturization have been the subject of extensive studies⁵, and circumventing anticipated limits involving manufacturing technology have been surprisingly innovative. This innovation has enabled the trend to continue much longer than was envisioned 10–20 years ago. To continue this progress, there are many challenging technological obstacles to overcome (see the ITRS). But the combination of many unforeseen difficulties projected to occur 10–15 years in the future has stimulated the imagination of researchers to explore new methods of fabrication, and the new properties of matter at nanometer dimensions. The hope is that sufficient knowledge for manufacturing appropriate structures, architectures, etc. at nanometer dimensions will extend the projection of Moore's Law substantially.

Stimulus from recognizing a technological challenge

For the last decade, predictions suggesting the end of this astonishing trend have been heard. Clearly a continuation forever is not expected; some technical limitations are very likely to arise as devices become smaller and smaller, if for no other reason than the size of the atom represents a limit as to how small circuits may become⁶. Imaginative predictions about the future may add some value to stimulating innovation, curiosity and thought; however, undisciplined exaggeration can misguide researchers in search of productive programmes. The opportunities offered by research in nanotechnology have been widely advertised; this has raised some criticism of hype related to these opportunities. The true limits of the technology are highly speculative and very important for the industrial world. Answers to key questions and the associated technological consequences represent an issue so important that a high degree of focus consistent with the principles of thermodynamics, kinetics and the laws of physics is a priority consideration.

One aspect of this challenge that has gained attention involves logic devices that may be effective at these dimensions. The transistor has been the key element allowing the architecture of today's computers. Complementary Metal Oxide Semiconductor (CMOS) technology is likely to continue the miniaturization trend for another decade, evidenced by the recent announcement by Intel of a terahertz transistor with dimensions approaching ten

nanometers⁷. Nevertheless, there has been considerable speculation about the possibility of fabricating transistors, alternative logic elements, or even molecular computers, from alternative structures and/or molecules⁸. This speculative area of research has raised considerable interest. In light of this speculation, the robust nature of the transistor and the need for a device having characteristics comparable to the transistor⁹ is noted. The electrical properties of molecules have been of considerable interest, in part due to this question. The conductivity of a single molecule has been measured, and surprising current–voltage relationships have shown negative differential resistance¹⁰ similar to that observed for resonant tunneling diodes. This two-lead device is unlikely to be a competitor to the transistor for logic, but it represents a surprising discovery illustrating complex molecular behaviour. The search for alternatives has generated considerable excitement that continues to date.

Stimulus from new instrumentation: New vistas for a frontier

Perhaps the most significant initial discovery leading to a rapid increase in understanding the properties of matter at the nanometer-level is the discovery of the scanning tunneling microscope (STM)¹¹. With the recognition that probes could be made sufficiently small to obtain atomic resolution, and that electrical current could be used to probe atomic environments, force microscopies and many other variations on proximal probes emerged to give additional data. Interest peaked rapidly with the arrival of these new tools. The discovery of the STM gained extremely rapid acceptance among several scientific disciplines, and was the basis for a Nobel Prize in Physics¹².

Stimulus from discovery of new scientific principles

In the same time frame, the discovery/recognition that the electrical conductance at nanometer dimensions is quantized¹³ suggested complexities with the behaviour of matter at these dimensions. Interference effects with electrical conductors¹⁴ also revealed the complexities of the wave nature of electrons with nanometer boundary conditions, and the non-traditional (non-classical) behaviour leading to new phenomena not associated with macroscopic material behaviour¹⁵.

In the same decade, the discovery of C₆₀, Buckminsterfullerene¹⁶, surprised the scientific world with the beautifully symmetric arrangement of sixty carbon atoms from an energetic plasma involving atoms and molecular fragments. This discovery gained rapid attention by a large segment of the chemistry and physics community, and also led to a Nobel Prize in Chemistry¹⁷. The fact that such order could result from interatomic forces began to

stimulate a realization that nature, itself, could be the source for the formation of well-organised nanostructures. In the same decade, the nature of the chemical bond for arranging more complex molecular geometries, and the use of non-bonding forces to form yet larger nanometer-dimensioned bits of matter, were demonstrated and led to a Nobel Prize in Chemistry¹⁸. Opportunities for 'self-assembly' began to be recognised, and this has become an occupation for a large number of chemists and biophysicists.

Stimulus from new materials

Subsequent to the discovery of the fullerenes, the discovery of the closely related carbon nanotubes stimulated still greater interest on the part of the scientific community¹⁹. These molecules were considerably larger than C₆₀, and demonstrated surprising properties. The strength of the perfect carbon fiber, when ultimately measured, indicated tensile properties exceeding those of steel by a factor of one hundred. Electrical conductivities were unusual, and demonstrated ballistic conduction over lengths exceeding one micron²⁰. The current densities carried by these perfectly cylindrical carbon nanotubes were surprisingly high. All of this stimulated considerable activity to understand the extent to which these remarkable properties could provide bulk materials with improved properties.

Biological organisms provide a wealth of materials for their use and protection. Examples such as spider silk (surprisingly strong) and the shell of a sea conch (which is amazingly tough) suggest alternative materials are available that we have not yet determined how to fabricate efficiently. Biological processes known only to the conch fabricate an intricate network of inorganic crystals aligned in one direction within a given layer, and an orthogonal direction in an adjacent layer. This intricate network of crystals is held together with a proteinaceous glue interspersed between the boundaries. The living organism excretes these materials oriented and in appropriate proportions for the resultant product.

Life processes have numerous examples involving the formation of nanostructures that are just beginning to be appreciated. The importance of non-bonding forces for self-assembly had been recognised in the structure of DNA²¹ for years, but the discovery of these alternative methods of self-assembly began to coincide with the ability to measure the properties with new tools, creating a synergism and new excitement in closely related fields. The fundamental aspects of these forces have led to a full series of publications involving papers in supramolecular chemistry²². Subsequent research involving the material pattern formation from intermolecular forces has been extensive and continues to expand rapidly. Exquisitely beautiful optical phenomena in nature illustrate examples

of self-assembled micro- and nano-structures resulting from evolutionary forces. The colours of insects (butterflies, moths, beetles, etc.) and of birds are due to chromophores and diffractive, interference and scattering phenomena from surprisingly complex structures²³ that provide mechanical strength to wing structures as well as the necessary capabilities to recognise the species, and even to regulate temperature.

New scientific frontiers: The integrated picture and the national nanotechnology initiative

Multiple events have converged to provide a persuasive argument for supporting a focus in nanotechnology: (i) successful historical trends and a projected end of this trend in the absence of new scientific principles, (ii) new research tools to explore a relatively unknown frontier, (iii) discovery of new phenomena with these tools, (iv) recognition (by example) of related superior products designed by nature, (v) advanced first-principle computational methods coupled with massive computational capabilities, and (vi) excitement over the possibility of new higher-performance products. These ingredients have fired the imagination of a broad coalition of scientists, engineers and venture capitalists envisioning expanded technological horizons. Coordination of the various constituencies has resulted in a surprisingly coherent voice supporting the scientific objectives, and an environment stimulating cooperation between scientists and private sectors searching for new ideas for new business opportunities.

This rich information frontier and motivated human resource offers unusual opportunities for expanding technological progress. This combination of events is ideal for focused scientific support at the political level. Higher-level coordination of technical programmes is something envisioned necessary by both scientists and political supporters. Credibility will be maintained through continual review by top-level scientific review and political oversight. The program has been well publicized, and is described in numerous documents^{24,25}.

Anticipated economic impact

The world economy may be estimated to have a total integrated annual gross domestic product of approximately \$31 trillion for the year 2001 (ref. 26). Estimates of the impact from advances emerging from nanotechnology developments over the next 15–20 years have been estimated by studies at the National Science Foundation, and total approximately \$1 trillion (see Table 2). In anticipation of this economic impact, nanotechnology research programmes in several countries have increased substantially in recent years. In the year 2002, it is estimated that government support for these programs approximates

SPECIAL SECTION: NANOSCIENCE AND NANOTECHNOLOGY

Table 2. Significant progress envisioned in traditional areas of importance

Area of importance	Envisioned impact	Potential economic impact ²⁷ (\$)
Electronics	Smaller devices, with greater density of information per unit volume/mass, greater processing speed, and consequently greater information processing, storage and retrieval capability foreseen.	300 B
Materials and chemicals	New materials anticipated with greater strength, toughness and shape memory effects, new magnetic materials, new materials with desirable optical properties, smart materials and composites by design. Advanced coatings to prevent environmental degradation. Improved catalysts for the production of a wide variety of industrially important materials are anticipated.	440 B
Biology, medicine	Sensors based on molecular interactions are very sensitive (with single molecule sensitivity and selectivity), especially important for biological purposes, DNA recognition, ... Drug delivery to specific sites (such as cancer cells) designed based on molecular interactions and nanometer-dimensioned delivery vehicles. Biologically compatible materials (bone, tissues) anticipated with improved understanding of structures at nanometer-level.	210 B
Energy, environment, transportation	Improved batteries, new methods for storing and converting energy are anticipated. Materials for filtering and trapping selected components are anticipated (filtering of water, cleaning up the environment). Materials for improved strength, lighter, more fuel efficient vehicles are anticipated.	135 B
Total estimated impact.		~ 1 Trillion

nearly \$2 B, of which \$600 M is included in the United States National Nanotechnology Initiative, administered by a number of government granting agencies.

Anticipated benefits of research in nanotechnology

The anticipated benefits from research in nanotechnology are outlined in Table 2, and are discussed in more detail below (see also ref. 27).

Electronics

Miniaturization of the logic and memory functions associated with computers continues with innovative discoveries as well as engineering finesse. The path to continued progress along these lines appears to be relatively certain with CMOS technology for another decade. Yet, beyond that time frame, there is a need for innovation that is not clearly spelled out. Nanostructures are also finding near-term utility in the area of electron field emission from cold cathodes, stimulating advances in flat panel displays and high-power microwave sources.

Memory

Miniaturization of electronic circuits has served as a stimulus for massive scientific and technological progress. Quantum wells, fabricated with nearly atomic precision and nanometer spacing²⁸, have been the basis of semi-

conductor devices (transistors, optical detectors) for many years. More recently, discoveries of giant magnetoresistance²⁹ (GMR) have served to reinforce the productivity of current research efforts and their impact on technological progress in this field. GMR is a direct product of fabricating ferromagnetic and diamagnetic layers with nanometer dimensions and precision. The current use of GMR in current magnetic disk memory units is increasing the capacity by an order of magnitude. The dimension of a bit on a magnetic disk is approaching that of the limiting dimension of a single domain (approximately 20 nm for iron), below which magnetic materials become superparamagnetic and permanent magnetization does not exist. Besides its use as a sensitive probe for magnetic fields, GMR materials exhibit hysteresis and may be used as a memory. Such memories are non-volatile, and represent the source of new computers where information may be retained in memory without power. The size of such 'MAGRAM' devices will be megabytes or greater, and is the subject of extensive research at present. Future magnetic memory devices are reviewed in a recent article³⁰.

An ultimate limit for the storage of information is the placement of a single atom. In 1990, Don Eigler, using a scanning tunneling microscope, demonstrated the ability to position individual atoms with this instrument³¹, achieving the ability to demonstrate this ultimate information density. Of course, the rate at which information may be stored and retrieved using this method is exceedingly slow, since it requires human manipulation of the individual atoms. The use of a single atomic force micro-

scope (AFM) for information storage parallels the principle of the old phonograph record, but with exceedingly higher spatial resolution. The speed of this process is relatively slow. However, this approach may be introduced with parallel read/write heads; with this arrangement, multiple channels read in parallel increases the rate of information transfer. This is the subject of the development by IBM with the 'millipede'³². The efforts of various information storage devices and systems is pictured in Figure 1, which shows the anticipated trend of greater information density at higher rates of storage and retrieval³³.

Other approaches involve measuring the electrical conductivity of molecules or molecular matter. Negative differential resistance of a molecule has already been mentioned¹⁰, and may be used as a memory element (although power is required to maintain a state). A recent patent demonstrates the use of crossbar architecture to measure the conductivity of a small amount of molecular material placed between two wires arranged in a grid³⁴. Application of an electrical field across the material between the wires changes the state of the matter and its conductivity. This is a result of hysteresis in the current-voltage relationship that may be used as a memory element. These only illustrate two principles for fabricating highly dense memories. Innovation is prolific in this field, and we can expect a number of alternative devices appearing in the relatively near term, with the usual market forces sorting out the successful products.

The energy required to place a charge on a capacitor is $(1/2)CV^2$, where C is the capacitance and V is the voltage. If the capacitance is small enough such that this energy approaches kT (the thermal energy, where k is the Boltz-

mann constant, and T is temperature), the voltage 'across' the capacitor increases stepwise with each electron. This is termed the 'coulomb blockade,' and serves as a possible memory device. Devices designed with this principle in mind (single electron devices, SEDs)³⁵ are envisioned for memory³⁶ as well as logic. A fundamental limitation involving these devices is due to the sensitivity of the device performance parameters to the presence of an electric field. Since any functioning system is envisioned to involve multiple SEDs adjacent to one another, the simple operation of one device will affect a neighbouring device, introducing complexities for compact architectures. The basic design, used with several electrons, however, may be viable as a high-density memory, and is being investigated extensively for this purpose.

Logic

New developments for logic represent a long-term challenge for nanotechnology. The transistor has dominated the heart of digital electronics due to the robust nature of the isolation of input signals from output and high gain, which allows fan out⁹. A large industry is currently poised for future developments to continue miniaturization trends, and no obvious contender to the silicon transistor is envisioned for the next 10–15 years. The ability to fabricate semiconductor structures with one-dimensional precision approaching atomic layer perfection provides researchers and industry with devices having nearly ideal behaviour for a 2-dimensional gas. This is illustrated in Figures 2a, b. Figure 2b illustrates the high frequency performance of InAs/AlSb HEMT, which is of value for high-frequency receivers/transmitters³⁷. Nevertheless, limitations to its use are predicted – simply because at some dimension silicon transistors will cease to operate.

Alternatives to semiconductors have been proposed for transistor logic. The discovery of conducting organic materials³⁸ introduced the possibility of fabricating devices from polymers and other organic structures, even molecules. This possibility has been pursued for almost two decades. Perhaps the most intriguing is that of the carbon nanotube, which demonstrates some amazing properties. The carbon nanotube (CNT), another form of elemental carbon, has generated a great deal of interest³⁹. Surprising mechanical and electrical properties have been measured for individual tubes. Transistor action has been observed with a back-gated CNT⁴⁰, and logical circuits have been demonstrated^{41,42}. More recently, transistors have been fabricated in the traditional design but a CNT has been substituted in place of a semiconductor conduction channel⁴³. The CNT is a structure that has no geometric irregularities, thus it offers surprisingly little impedance to the flow of electrons along its axis. The resulting transistor has a higher transconductance (per unit width of con-

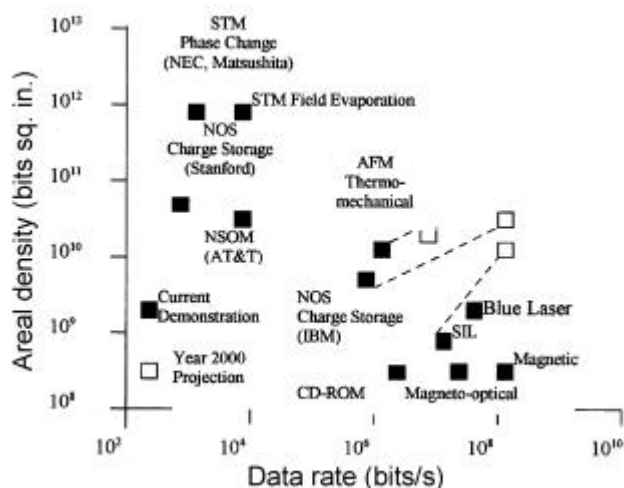


Figure 1. Approaches to high density recording. Relationship between information density and speed of storage/retrieval for several devices. (STM, Scanning tunneling microscopy; AFM, Atom force microscopy; NOS, Nitride oxide semiconductor structures; NSOM, Near-field scanning optical microscopy; SIL, Solid immersion lens) (Mamin, H. J. *et al.*³³).

duction channel) than traditional silicon transistors. The challenge of fabrication and assembly of millions of these in perfect order, however, represents a major hurdle for effective commercial utilization. The problems involving interconnects, heat dissipation, cross-talk, statistical irregularities in structures, and conventional noise sources that are challenging with conventional digital electronic devices, will continue to represent major hurdles with smaller devices.

Perhaps even further in the future are concepts emerging from phenomena involving cellular automata. Elements of an array may perform certain logical operations based on the state of neighbouring elements. A large interconnected array of such elements will evolve with time according to the local interactions. Applied to nanostructures, where quantum phenomena are typically involved, the behaviour of quantum cellular automata has been the subject of numerous investigations⁴⁴. Inherent in this idea is an array of atoms and charges that relax to their lowest state after an impulse represented by a set of bits. As these arrays increase in size, the energy spacing between

states becomes smaller, limiting the usefulness of the solutions due to thermal occupation of closely spaced higher energy states.

Cold cathode emission

The ubiquitous cathode ray tube is being displaced with newer flat-panel display devices. One of the approaches to display panels involves electron field emission from cold emitters. With the sharp features of carbon nanotubes, along with their conductivity and rugged mechanical properties, these materials have been examined extensively lately⁴⁵ for this purpose. A thin film transistor fabricated with a random network of single wall nanotubes and the electron mobility of the device⁴⁶ is illustrated in Figure 3 as an example of the degree of control possible with these nanostructures. The same phenomenon that allows greater electron emission for display purposes can be used to fabricate cold cathodes for improved high power, high frequency microwave sources such as gyrotrons⁴⁷.

Communication

With the advent of higher frequency computers, sophisticated processing of information is increasingly possible. This, in itself, presents substantial advantages for enhanced speed. High power microwave sources represent opportunities for communication. But, in addition, optical communication is being enhanced with new materials that offer properties based on nanometer-scale fabrication. Optical band gap materials may be fabricated with appropriately modulated index of refraction in materials. One of the more exotic ways to fabricate such materials involves self-assembly processes with block co-polymers⁴⁸. New and inexpensive sources of such materials serve to stimulate high performance communication networks and an ever-increasing availability of information.

Materials

The basis of every substantive device with which we interact involves a material. This is exactly where the opportunities lie with nanostructures, since they are materials at the most fundamental level above that of an atom or molecule. Materials may be classified based on the method of fabrication. Different professional communities have become identified with alternative methods for fabricating materials. The pursuit of new nanostructured materials by different means has altered the usual professional community identification with beneficial and innovative products.

Without reference to use, a number of papers have demonstrated the fabrication of a remarkable number of

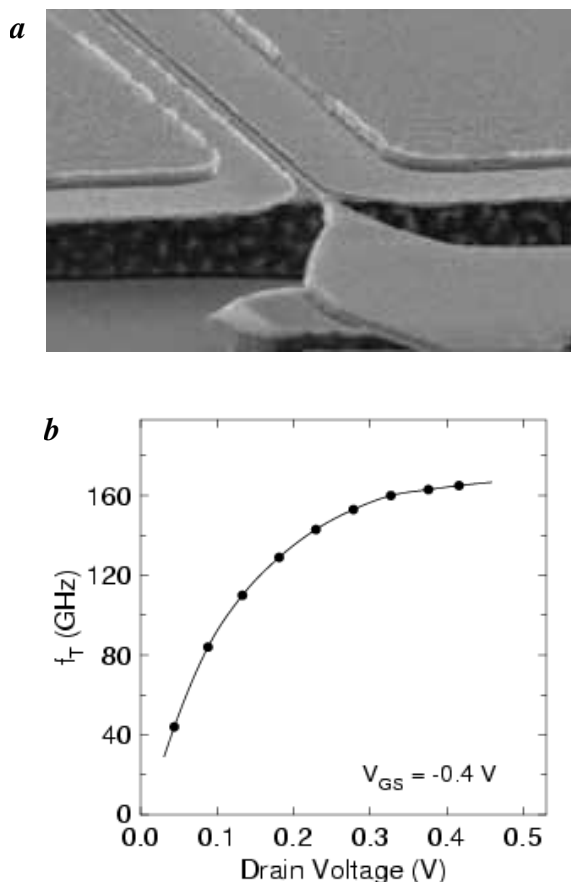


Figure 2. *a*, Scanning electron microscope image of the high frequency InAs/AlSb HEMT with $L_g = 60$ nm (ref. 83). *b*, Illustration of the high frequency performance of InAs/AlSb HEMTs with $L_g = 60$ nm at low drain voltages.

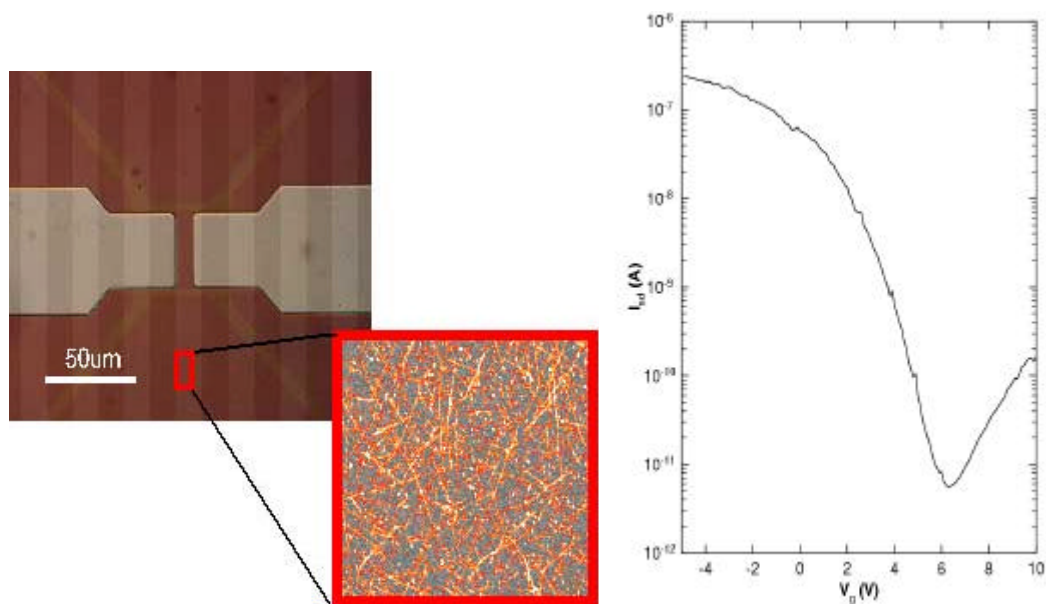


Figure 3. Thin-film transistor composed of a random network of single-wall C nanotubes. The electron mobility of the nanotube network is about 10 times higher than commercial thin-film transistors. The networks can be deposited onto arbitrary substrates and patterned using conventional microprocessing techniques (Snow, E. S. *et al.*⁴⁶).

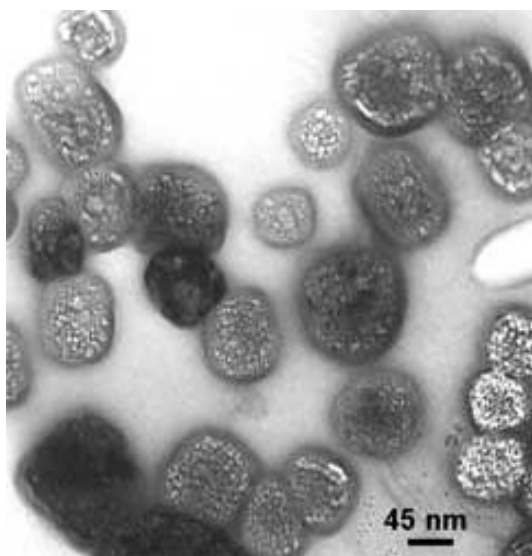


Figure 4. TEM micrograph of Co/Co(OH)₂ particles formed inside polymerized vesicles. Palladium ion bound to negatively charged phospholipids in the membrane initiated electroless metallization on the vesicle surface following diffusion of Co plating bath through the polymerized membrane (Markowitz, M. A. *et al.*⁴⁹).

fascinating nanoparticles with many different methods. These are too numerous to review here, and examples are ubiquitous. Methods for fabricating nanopowders and/or colloidal particles include: (i) extensive ball milling, (ii) condensation or precipitation, (iii) drawing glassy materials, (iv) self-assembly (this includes biological fabrication), (v) forming materials around/within templates, and (vi) growth of a second material on a crystalline lattice in

which the lattice parameters do not match (strained layer growth). A TEM micrograph shown in Figure 4 illustrates formation of nearly uniform size particles of Co/Co(OH)₂ inside polymerized vesicles⁴⁹. Some materials form naturally in the form of porous arrays. One such material is that of sol gels, when solvent is removed. Figure 5 shows Au nanoparticles functionalized with cytochrome C in a mesoporous silica aerogel host. The monodispersity of this method appears to give surprisingly monodisperse nanoparticles, reported to be about 5% of mean particle size.

An inspiration for new materials involving nanostructures comes from several directions: (i) traditional metallurgical research, (ii) biological materials and functions, (iii) organic materials (such as plastics), and (iv) optimization of optical properties.

Alloys, ceramics, composites

Traditional materials scientists pursuing materials for increased strength have noted improved alloy strength and ductility as crystallite size decreases (this trend is reversed at sufficiently small dimensions). Superplasticity (very large tensile deformations) may be obtained with very small crystal grains. The inverse relationship between strength and crystal size is referred to as the Hall-Petch relationship⁵⁰, and has been the basis for new alloy design for decades. Methods such as rapid solidification, rapid cooling of vapours, and severe plastic deformation have been used with increasing success to produce nanostructured grain sizes. With new tools for obtaining high definition information about nanostructures, understand-

ing these phenomena has opened new frontiers for understanding this traditional path to important materials^{51,52}. A word of caution is inserted for finely structured alloys. At higher temperatures during consolidation or sintering processes, the smaller grain sizes tend to be consumed by the larger grain sizes referred to as grain growth. This 'ripening' leads to a reduction of the advantages associated with the use of these materials. Nevertheless, opportunities continue to emerge.

Ceramics are generally fabricated with a heating and sintering process. The finer the constituent powder, the easier it is to prepare materials with a uniform and dense structure. Many techniques may be used to fabricate these fine powders. High energy ball milling has been found to yield fine nanopowders, especially of oxides that are basically brittle and thermodynamically stable. The sol gel method has been used to fabricate a wide range of powders with nanometer dimensions. Ceramics formulated with nanometer crystal grains do not inherently scatter light, and may appear as clear ceramic structures. The increased ductility of these ceramics allows them to be molded with increased ease.

Composites have demonstrated their utility in many useful materials. With nanostructured materials incorporated to design various composites, many new applications have been found. Naturally occurring nanostructured materials such as montmorillonite (a layered aluminosilicate) are introduced into a variety of plastics to form stronger structural materials used widely in the building industry and elsewhere. Nanostructured calcium carbonate is another frequently used nanopowder added to form composites. The mechanical properties of carbon nano-

tubes have been intriguing ever since they were recognized as another 'perfect' form of carbon fiber. The tensile strength of multiwalled carbon nanotubes has been measured to be approximately 45 GPa⁵³, many times that of high strength steels. Measurements on single-walled carbon nanotubes give yield strengths of approximately the same value⁵⁴. The challenge to produce a practical composite material with these nanotubes involves an appropriate dispersal in a matrix, along with suitable treatment to provide adherence between the nanotube and the surrounding matrix material. This challenge is currently the subject of intense laboratory research.

Coatings

The greater structural integrity of closely packed and/or sintered nanoparticles gives coatings based on these materials improved adhesive and cohesive properties for many applications. Processes include electrochemical and electroless deposition, thermal spray, and simple painting of a precursor with subsequent treatment to obtain hardness, wear resistance and improved corrosion resistance.

Catalysts

Although not a new endeavour, the challenge of transforming materials into useful products is enhanced greatly with the aid of suitable catalysts. The mechanisms by which catalysts are effective have remained a mystery for decades, although with tools now becoming available such as those in the repertoire of nanotechnology, much greater insight is emerging for this important industry. The ability to fabricate catalysts with greater surface area is inimitably tied to fabrication of smaller particle sizes for catalysts. In addition, smaller particle sizes may expose selected crystal faces in greater abundance, representing modified activity for a given catalyst. Fuel cells are critically dependent on appropriate catalysts and membranes (another nanostructured material); these materials are gaining much greater attention today as this source of energy becomes increasingly important for portable power.

One form of catalyst used extensively in the petroleum industry is that of zeolites (silicates and aluminosilicates), which are structured with pores and channels having the 'right' dimensions to encase selected molecules for catalytic activity (hence they may be specific to certain chemicals). These materials may also be used as molecular sieves and exchange ion catalysts. The sol gel method has been shown to yield, under appropriate conditions, a wide variety of nanoporous structures where the dimensions of the pores may be varied depending on the starting material and treatment conditions.

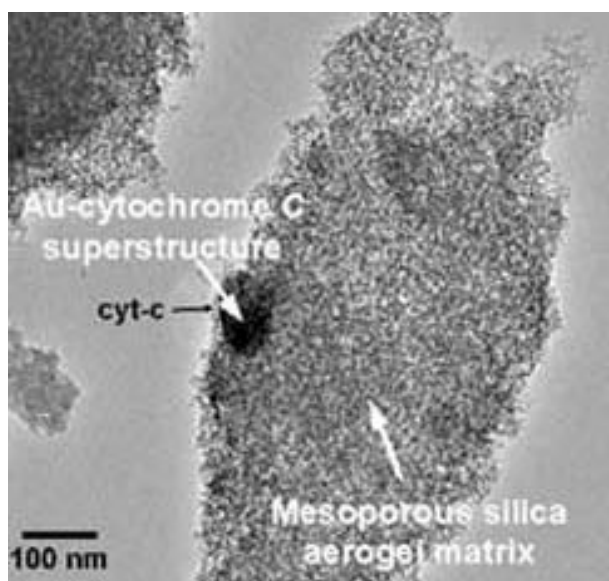


Figure 5. Cytochrome C retains bio-activity in mesoporous silica aerogel host. (Courtesy of Jean-Marie Wallace, Jeremy Pietron, Jane Rice, Debra Rolison and Rhonda Stroud, Naval Research Laboratory.)

Biological materials

The mysteries of life are tied up in the sequence of amino acids in DNA. The DNA double strand is held together through non-chemical bonding forces (hydrogen bonding, dipolar coupling, van der Waals forces). DNA is just one example of the great variety of molecular components in life's processes that follow an exquisitely complex sequence of chemical reactions. From the functioning, living organism, to the functions of each organ, each cell, to self-assembled lipid bilayers composing the structure of the living cell⁵⁵, to more refined molecular structures⁵⁶, the ability of life to assemble structures in a hierarchical manner to form macroscopic products having such intricate functions⁵⁷ will be a source of discovery for years in the future.

Organic materials may exert a significant influence in the formation of inorganic materials, a fact that nature has introduced with the production of shells of crustaceans. A recent case illustrating this principle is one in which proteinaceous materials have been isolated that have a significant influence on the morphology of nanostructures of gallium arsenide⁵⁸ as it is formed. An initial complex mixture consisting of many peptides was placed in contact with gallium arsenide nanostructures, the bulk liquid removed, and the peptides adhering to the crystalline surfaces were isolated. This mixture was amplified by polymerase chain reaction⁵⁹ (PCR) techniques and again exposed to gallium arsenide. Several cycles effectively selected and amplified those peptide species that adhered tightly to the solid surface, and even to a specific face of the crystalline solid surface. These peptide materials have been shown to significantly alter the morphology of crystallite formation for III-V and II-VI materials. The implications of this approach are just beginning to be realized.

Optical materials

Scattering of nanoparticles in ordinary visible light is minimal due to the much smaller dimension of the particle. Absorbance is the dominant mechanism for extinction of optical radiation, and dispersions of nanoparticles have been used for years as a sunscreen. Luminescence of quantum dots can be quite efficient; the wavelength of this luminescence is strongly influenced by the dimension of the particle. By decorating nanoparticles of materials such as CdS and CdSe with biologically active molecules, these particles are found to be effective labels for examining functions in cells⁶⁰ or for labeling or identifying sites in a protein chain⁶¹. The narrow emission lines that may be tuned by altering the dimensions of the particles offers distinct advantages over conventional staining and labeling methods. Higher technology applications of quantum dots are envisioned. A sought-after

goal is to assemble an array of monodisperse quantum dots that will provide gain and hence an efficient optical laser with minimal energy requirements and high efficiency.

Successful band gap tailoring of nanolayered semiconductors has given rise to laser sources of commercial importance today. Vertical Cavity Surface Emitting Lasers (VCSELs) have become a source of light for CD data storage. More recently, quantum cascade lasers have been introduced⁶² and have already found commercial acceptance as infrared sources for spectroscopically sensing for environmental pollutants.

Self-assembly

Just how nature provides living organisms with the ability to fabricate intricate nanostructured materials such as silk, elastin and collagens is a mystery. However, it is apparent that assembling such patterns is built into selected processes in nature at the most fundamental level⁶³. The structure of a crystal is quite regular, and is the result of interatomic forces and a minimization of the energy (with entropy concerns) of the system. Larger molecular units also assemble in specific patterns. Research at the intersection of chemistry, materials and biotechnology is providing a rich library of molecular and particle interactions and a new source for a great variety of new materials. The concept of 'self-assembly' has become recognized as a major research frontier^{64,65}. Life, itself, is assumed to be the end product of self-assembled hierarchical structures. Thus, the vast number of combinations among atoms and molecules that may lead to self-assembled materials has been selected by the criterion of self-replication (a dominant function of life). If one were to apply a different criterion for selection (such as material strength, or certain desired optical properties), this suggests that there are a great variety of materials that may be obtained by making use of self-assembly under conditions not optimized for life processes⁶⁶.

Recognition of the vast array of new materials that may be formed with non-bonding attractive forces, a new discipline is emerging. Just as atoms combine to form molecules, molecules combine to form larger aggregates. Research in the area of supramolecular chemistry is the basis for a journal series²², indicating the volume of work beginning to emerge from this field. In fact, just as the formation of the chemical bond formed the basis for a century of progress (understanding synthesis, properties, and product development), we may be on the verge of another century of progress during which we learn to understand how to take advantage of supramolecular complexes and self-assembly. It is, at the least, the basis for the formation of biological molecules, and most likely, much more.

Recognizing the strong tendency for individual DNA strands to self-assemble into appropriate sequences, innovative approaches have emerged to take advantage of this fact. One such example involves the fabrication of coloured displays. One type of flat panel display uses vertical cavity surface-emitting lasers (VCSELs)⁶⁷. By energizing a suitable pattern of red, green and blue VCSELs, colour images may be formed. The challenge is to place VCSELs, fabricated by a separate process, in the correct places. This has been solved by placing a clearly defined yet different DNA sequence on each VCSEL for a given colour. A complementary DNA sequence is placed on the base panel where the VCSELs are to be located. By introducing the labelled VCSELs in a fluid in contact with the patterned panel, the DNA complementary strands are attracted to one another, and serve the function of placing the VCSELs in appropriate locations⁶⁸. Sub-micron placement over dimensions of a meter or more has been achieved with this process.

Energy

An additional material that has gained remarkable recognition lately is that of the carbon nanotube^{69,70}. Past success with incorporating micron-sized carbon fibers into composite materials for strength and for varying conductivity has suggested a reason for substantial interest in this material. But the high strength of the individual carbon nanotubes themselves (ten times that of steel) and the unusual conductivity⁴² has generated a major thrust to fabricate and take advantage of these unusual properties. Carbon nanotubes have been proposed for many other technological solutions, such as making a good source of hydrogen storage, although several measurements of this capability have yielded conflicting measures of merit⁷¹. Various metallic alloys have also appeared promising for hydrogen storage; it stands to reason that smaller particle grain sizes offer a greater surface area for hydrogen gas entering the immediate surface with such storage phenomena. Carbon nanotubes store lithium in a ratio of 3:1, C:Li (or better), a higher density than for ordinary graphite^{72,73}, making it a promising anode material for battery applications.

Sensors

The exquisite sensitivity and selectivity developed for characterizing nanostructures may be used as a probe of intermolecular interactions. Since specific molecules (true particularly of large molecules) tend to be selectively attracted to other molecules having a complementary structure, this selective interaction may be designed to yield a sensitive measure of the presence of a particular mole-

cule. Many schemes have been developed for these purposes.

One approach used successfully for years is that of pregnancy testing. In this test, gold nanoparticles are coated with molecular species capable of detecting the presence of antibodies that appear when a person is pregnant. When the specific antigen appears in solution, the coated gold particles agglomerate through forces linking the antibodies to the coating on the gold. Agglomerated gold particles appear optically to have a different colour than the same gold particles in suspension. The simple test of a change in colour is sufficient to provide a reliable test for pregnancy. Taking the effect of a specific molecule on coated gold particles further, coated particles will settle between electrodes coated with complementary oligonucleotides, changing the conductivity between electrodes⁷⁴. This represents an electrical detection of the same attractive forces that lead to agglomeration and a change of colour in the first example.

A clever scheme has made use of the sensitive detection involving giant magnetoresistance⁷⁵. Small iron (or other permanent magnetic material) particles are coated with a molecular material matching the sequence of a selected protein. In the presence of the selected protein, binding occurs, leaving a different molecular sequence at the edge of the magnetic particles. A second template of giant magnetoresistive strips is coated with the molecular sequence complementary to those now coating the magnetic particle. When the coating on the magnetic particle comes in contact with that on the magnetoresistive strip, binding occurs, placing the magnetic particle in close proximity with the metallic strip, altering the conductivity of the strip. This may be detected by simple measure of resistance between two contacts as shown schematically in Figure 6. This device is named the Bead ARray Counter (BARC). An array of these detectors is able to detect the number of binding events. If, alternatively, an array is coated with molecular sequences for a variety of analysts, the presence of any of a variety of substances may be detected based on the response of each area of the array.

Biological/medical opportunities

Of all the beneficiaries of this scientific revolution, the biological and medical sciences will reap many of the earliest fruits of this research⁷⁶. Biological molecules, by virtue of their size, may be classified as nanostructures. The interaction among the complex mechanisms of life may be seen as simply chemistry, or as specialized interactions between nanostructures. The sensitive tools that measure the presence of a single chemical bond, or attractive forces between molecular arrays having dipolar forces correctly aligned, provide exceptional information about the presence of forces between highly selective biological molecules.

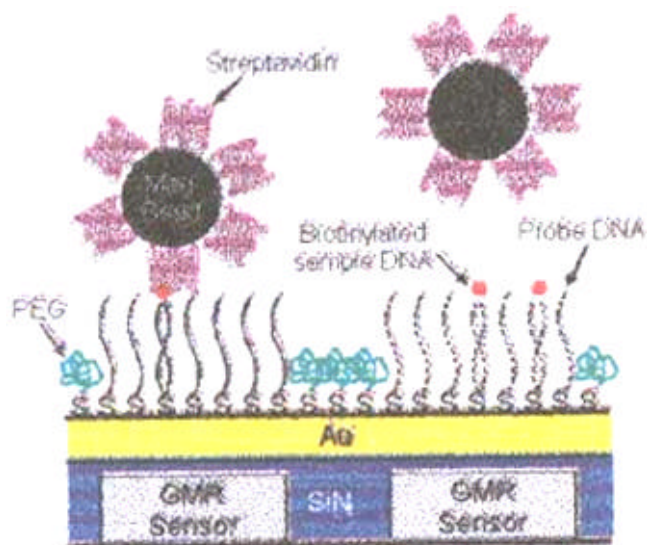


Figure 6. A revolutionary biosensor for the simultaneous detection of multiple biological warfare agents. The Bead ARray Counter (BARC) combines state-of-the-art magnetic materials with DNA-based biotechnology on a single sensor microchip. When DNA molecules from a biowarfare agent such as anthrax are present, miniature magnetic beads are captured onto the chip surface. These beads are counted by arrays of sensitive magnetic field sensors made of a special 'giant magnetoresistive' alloy (the same type of material behind the rapid increase in computer hard-disk capacity). Because each sensor can detect a single magnetic bead, in theory, the BARC biosensor could detect a single molecule of DNA from a lethal agent. (Courtesy: Whitman, L., Naval Research Laboratory).

DNA chips^{77,78} represent a technology that developed simultaneously with the emergence of nanotechnology as an initiative. Although developed separately, the principles involved fall directly in line with those espoused by the nanotechnology initiative. DNA segments that match selected complementary patches of DNA on a 'chip' bind with one another, creating an environment that modifies the luminescence of a particular site in an array of DNA segments. The matching sites provide clear information about the structure of an unknown sample of DNA segments.

Medicines may be incorporated in the heart of nanostructures for selected delivery in a living species. These medicines may be encapsulated in solid-state nanoparticles for time-release delivery⁷⁹, or in specialized molecular shells that have been decorated with antibody/antigen or complementary protein molecular patterns. These specialised shells are attracted to specific kinds of cells in a living species, such as cancer cells, providing a carefully selected delivery mechanism for the contents of these nanoparticles.

Artificial living tissues represent yet another opportunity for fabricating new materials that are compatible with those of living species. Bone, for example, may be replaced with materials such as hydroxyapatite⁸⁰. The effectiveness of such tissue transplants depends not only on the crystallite structure of the underlying material, but also on the surface layers interacting with living tissue.

Learning how to fabricate such structures is a challenge undertaken for many years without the assistance of the new tools becoming available today. Progress should be substantially greater with the insight afforded by these new tools.

Theory

Theoretical predictions of atomic and molecular behaviour have been improving for several decades. Quantum mechanics forms the basis for extensive models giving increasingly useful predictions about behaviour at the atomic and molecular scale. Macroscopic behaviour, of course, is modeled with numerical techniques such as finite element methods, giving good approximations for bulk behaviour. Models for particles and interactions at nanometer dimensions, however, are a greater challenge. The number of particles is substantially larger than for a molecule, and quantum mechanical models involve extensive computational time for these larger particles. Nevertheless, with improved models, predictions of the behaviour of nanoparticles are becoming useful adjuncts to experimental observations, and provide useful guidelines for experiments.

An early prediction that carbon nanotubes would be conducting was made from quantum mechanical models before these particles had been measured⁸¹. The properties of a 2-dimensional electron gas are highly dependent on a smooth interface between adjacent layers of two different semiconducting materials. The disorder at the interface is a function of the energy differences between exact atomic placement and that where disorder is present. Predictions of the degree of disorder have been successful lately, for a number of heterostructures including quantitative evaluation of stacking fault density at the interface on spin injection efficiency in a semiconductor spintronic system such as ZnMnSe/AlGaAs-GaAs⁸².

Summary

Nanotechnology as a scientific and technological thrust encompasses the best of many opportunities afforded to the scientific, engineering, and industrial communities. The scientific opportunities appear to be considerable, industrial interest is high, and the social benefits are significant from new materials, and new products applicable to information technology, medicine, energy and the environment. It deserves support where the objectives can be justified based on their scientific and technological merits, and it provides a vision for transitioning new discoveries to products. The only word of caution associated with this bright frontier is: Decisions must be based on sound scientific merit having experimental evidence and/or valid theoretical foundation combined with a realistic assessment of the challenges that must be met to fulfill the promise.

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