

Introduction

1. Introduction to Nanotechnology

A biological system can be exceedingly small. Many of the cells are very tiny, but they are very active; they manufacture various substances; they walk around; they wiggle; and they do all kinds of marvelous things—all on a very small scale. Also, they store information. Consider the possibility that we too can make a thing very small that does what we want—that we can manufacture an object that maneuvers at that level.

(From the talk "There's Plenty of Room at the Bottom," delivered by Richard P. Feynman at the annual meeting of the American Physical Society at

1.1	Nanotechnology – Definition and Examples	1
1.2	Background and Research Expenditures .	4
1.3	Lessons from Nature (Biomimetics)	6
1.4	Applications in Different Fields	7
1.5	Various Issues	8
1.6	Research Training	8
1.7	Organization of Handbook	9
	References	9

the California Institute of Technology, Pasadena, CA, on December 29, 1959.)

1.1 Nanotechnology – Definition and Examples

Nanotechnology literally means any technology done on a nanoscale that has applications in the real world. Nanotechnology encompasses the production and application of physical, chemical, and biological systems at scales ranging from individual atoms or molecules to submicron dimensions, as well as the integration of the resulting nanostructures into larger systems. Nanotechnology is likely to have a profound impact on our economy and society in the early 21st century, comparable to that of semiconductor technology, information technology, or cellular and molecular biology. Science and technology research in nanotechnology promises breakthroughs in areas such as materials and manufacturing, nanoelectronics, medicine and healthcare, energy, biotechnology, information technology, and national security. It is widely felt that nanotechnology will be the next industrial revolution.

Nanometer-scale features are mainly built up from their elemental constituents. Examples include chemical synthesis, the spontaneous self-assembly of molecular clusters (molecular self-assembly) from simple reagents in solution, biological molecules (e.g., DNA) used as building blocks for the production of three-dimensional nanostructures, or quantum dots (nanocrystals) of arbitrary diameter (about 10 to 10⁵ atoms). The definition of

a nanoparticle is an aggregate of atoms bonded together with a radius between 1 and 100 nm. It typically consists of 10 to 10⁵ atoms. A variety of vacuum deposition and nonequilibrium plasma chemistry techniques are used to produce layered nanocomposites and nanotubes. Atomically controlled structures are produced using molecular beam epitaxy and organometallic vapor phase epitaxy. Micro- and nanosystem components are fabricated using top-down lithographic and nonlithographic fabrication techniques and range in size from micro- to nanometers. Continued improvements in lithography for use in the production of nanocomponents have resulted in line widths as small as 10 nm in experimental prototypes. The nanotechnology field, in addition to fabrication of nanosystems, provides impetus to develop experimental and computational tools.

The discovery of novel materials, processes, and phenomena at the nanoscale and the development of new experimental and theoretical techniques for research provide fresh opportunities for the development of innovative nanosystems and nanostructured materials. The properties of materials at the nanoscale can be very different from those at a larger scale. When the dimension of a material is reduced from a large size, the properties remain the same at first, then small changes occur, until finally, when the size drops below 100 nm, dramatic

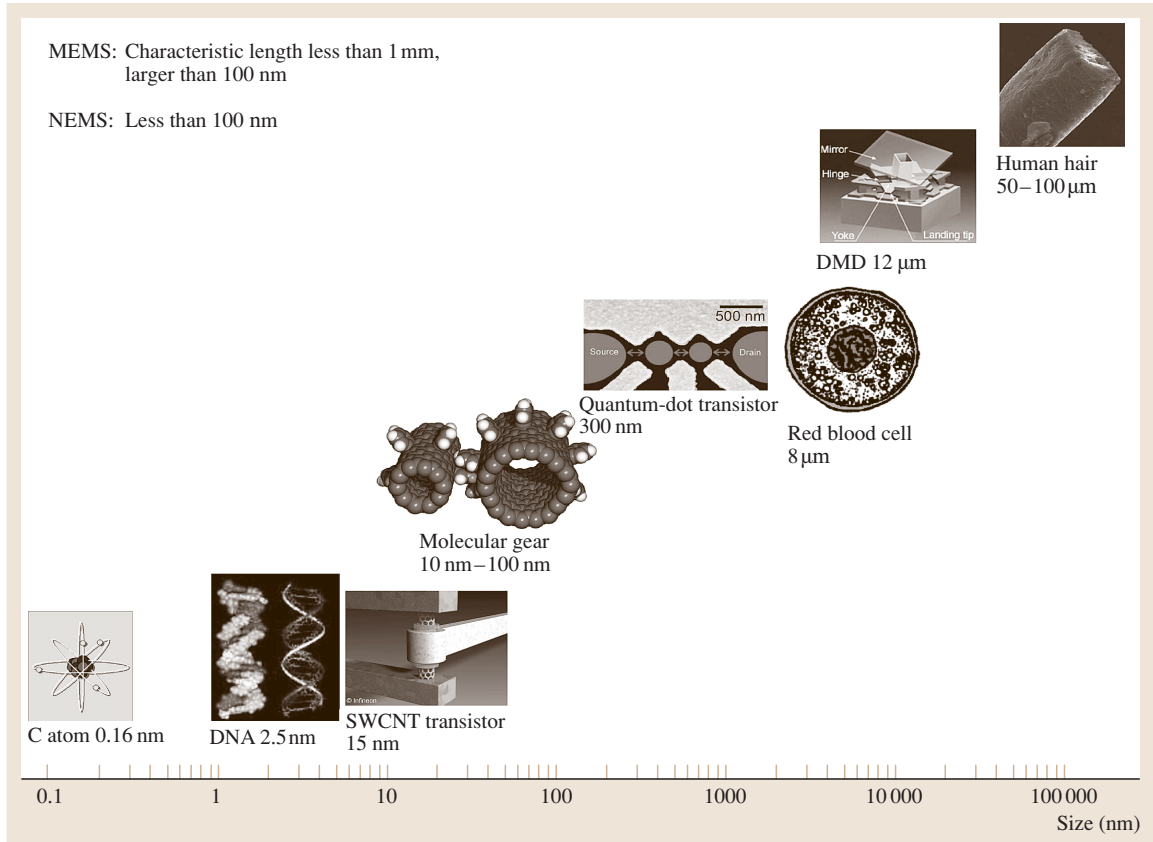


Fig. 1.1 Dimensions of MEMS and NEMS in perspective. MEMS/NEMS examples shown are of a vertical single-walled carbon nanotube (SWCNT) transistor (5 nm wide and 15 nm high) [1.1], of molecular dynamic simulations of a carbon-nanotube-based gear [1.2], quantum-dot transistor obtained from [1.3], and DMD obtained from www.dlp.com

changes in properties can occur. If only one length of a three-dimensional nanostructure is of nanodimension, the structure is referred to as a quantum well; if two sides are of nanometer length, the structure is referred to as a quantum wire. A quantum dot has all three dimensions in the nanorange. The word quantum is associated with these three types of nanostructures because changes in properties arise from the quantum-mechanical nature of physics in the domain of the ultra small. Materials can be nanostructured for new properties and novel performance. This field is opening new venues in science and technology.

Micro- and nanosystems include micro/nanoelectromechanical systems. MEMS refers to microscopic devices that have a characteristic length of less than 1 mm but more than 100 nm and combine electrical and mechanical components. NEMS refers to nanoscopic devices that have a characteristic length

of less than 100 nm and combine electrical and mechanical components. In mesoscale devices, if the functional components are on a micro- or nanoscale, they may be referred to as MEMS or NEMS, respectively. These are referred to as intelligent miniaturized systems comprising sensing, processing, and/or actuating functions and combine electrical and mechanical components. The acronym MEMS originated in the USA. The term commonly used in Europe is microsystem technology (MST), and in Japan it is micromachines. Another term generally used is micro/nanodevices. MEMS/NEMS terms are also now used in a broad sense and include electrical, mechanical, fluidic, optical, and/or biological functions. MEMS/NEMS for optical applications are referred to as micro/nanooptoelectromechanical systems (MOEMS/NOEMS). MEMS/NEMS for electronic applications are referred to as radio-

Table 1.1 Dimensions and masses in perspective. (a) Dimensions in perspective

NEMS characteristic length	< 100 nm
MEMS characteristic length	1 mm and > 100 nm
Molecular gear	≈ 10 nm
Vertical SWCNT transistor	≈ 15 nm
Quantum-dots transistor	300 nm
Digital Micromirror	12 000 nm
Individual atoms	Typically fraction of a nm in diameter
DNA molecules	≈ 2.5 nm wide
Biological cells	In the range of thousands of nm in diameter
Human hair	≈ 75 000 nm in diameter

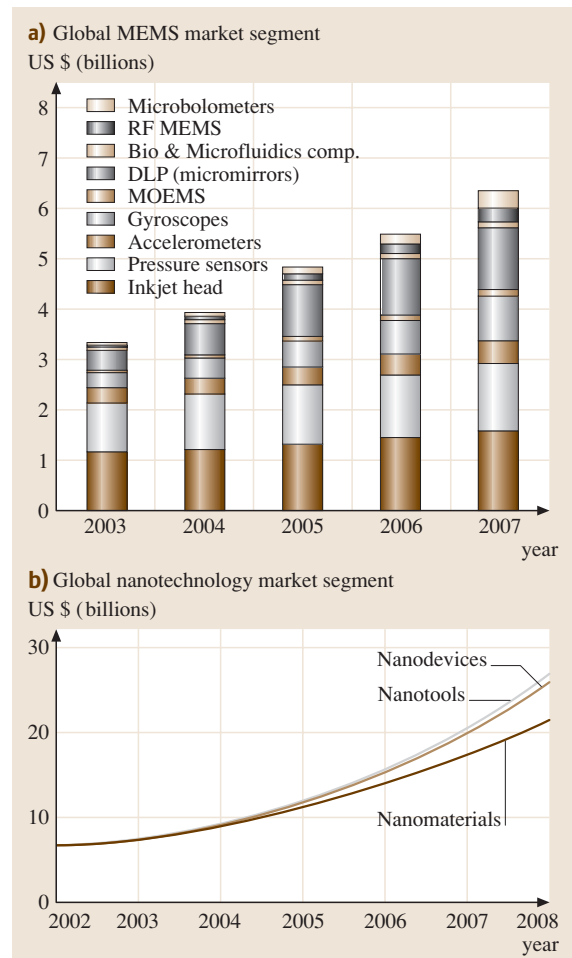
Table 1.2 (cont.) (b) Masses in perspective

NEMS built with cross sections of about 10 nm	As low as 10^{-20} N
Micromachines silicon structure	As low as 1 nN
Water droplet	≈ 10 μ N
Eyelash	≈ 100 nN

frequency-MEMS/NEMS or RF-MEMS/RF-NEMS. MEMS/NEMS for biological applications are referred to as BioMEMS/BioNEMS.

To put the dimensions of MEMS and NEMS in perspective, see Fig. 1.1 and Table 1.1. Individual atoms are typically a fraction of a nanometer in diameter, DNA molecules are about 2.5 nm wide, biological cells are in the range of thousands of nanometers in diameter, and human hair is about 75 μ m in diameter. The NEMS shown in the figure range in size from 15 to 300 nm and MEMS is 12 000 nm. The mass of a micromachined silicon structure can be as low as 1 nN, and NEMS can be built with a mass as low as 10^{-20} N with cross sections of about 10 nm. In comparison, the mass of a drop of water is about 10 μ N, and the mass of an eyelash is about 100 nN.

MEMS and emerging NEMS are expected to have a major impact on our lives, comparable to that of semiconductor technology, information technology, or cellular and molecular biology [1.4, 5]. MEMS/NEMS are used in electromechanical, electronics, information/communication, chemical, and biological applications. The MEMS industry in 2004 was worth about \$4.5 billion and with a projected annual growth rate of 17% (Fig. 1.2) [1.6]. Growth of Si-based

**Fig. 1.2** Global MEMS and nanotechnology market segments

MEMS may slow down, and nonsilicon MEMS may pick up during the next decade. The NEMS industry was worth about \$10 billion dollars in 2004, mostly in nanomaterials (Fig. 1.2) [1.7]. It is expected to expand in this decade, in nanomaterials, biomedical applications, and nanoelectronics or molecular electronics. For example, miniaturized diagnostics could be implanted for early diagnosis of illness. Targeted drug delivery devices are under development. Due to the enabling nature of these systems and because of the significant impact they can have on both commercial and defense applications, industry as well as federal governments have taken a special interest in seeing growth nurtured in this field. MEMS/NEMS are the next logical step in the “silicon revolution.”

1.2 Background and Research Expenditures

On December 29, 1959 at the California Institute of Technology, Nobel Laureate Richard P. Feynman gave a talk at the annual meeting of the American Physical Society that has become a classic in 20th-century science lectures. The talk was titled “There’s Plenty of Room at the Bottom” [1.8]. He presented a technological vision of extreme miniaturization in 1959, several years before the word “chip” became part of the lexicon. He talked about the problem of manipulating and controlling things on a small scale. Extrapolating from known physical laws, Feynman envisioned a technology using the ultimate toolbox of nature, building nanoobjects atom by atom or molecule by molecule. Since the 1980s, many inventions and discoveries in the fabrication of nanoobjects have

been testament to his vision. In recognition of this reality, in 1998 the White House National Science and Technology Council (NSTC) created the Interagency Working Group on Nanoscience, Engineering, and Technology (IWGN). In a January 2000 speech at the same institute, former President Bill Clinton talked about the exciting promise of “nanotechnology” and, more broadly, the importance of expanding research in nanoscale science and technology. Later that month, he announced in his State of the Union Address an ambitious \$497 million federal, multiagency national nanotechnology initiative (NNI) in the 2001 fiscal year budget and made the NNI a top science and technology priority [1.9, 10]. The objective of this initiative was to form a broad-based coalition in which academia, the private sector, and local, state, and federal governments would work together to push the envelope of nanoscience and nanoengineering to reap nanotechnology’s potential social and economic benefits.

Funding for this initiative in the US has continued to rise. In January 2003, the US Senate introduced a bill to establish a National Nanotechnology Program. On

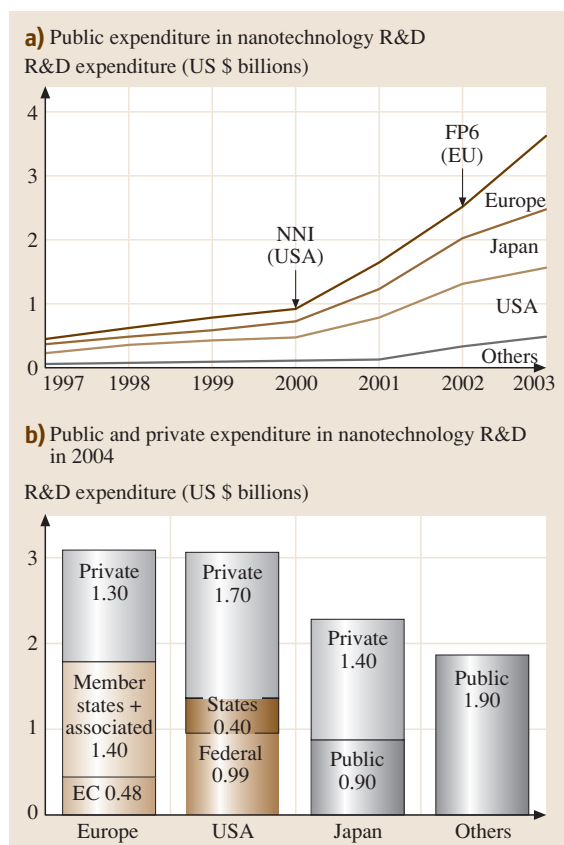


Fig. 1.3a,b Breakdown of public expenditure in nanotechnology R&D (a) around the world (source: European Commission 2003) and (b) by public and private resources in 2004 (source: European Commission 2005; private figures based upon Lux Research)

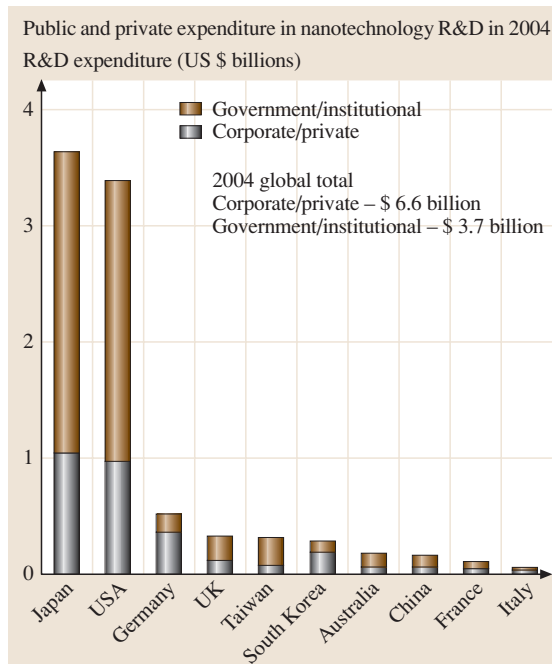


Fig. 1.4 Breakdown of public and private expenditures in nanotechnology R&D in 2004 in various countries (Lawrence 2005)

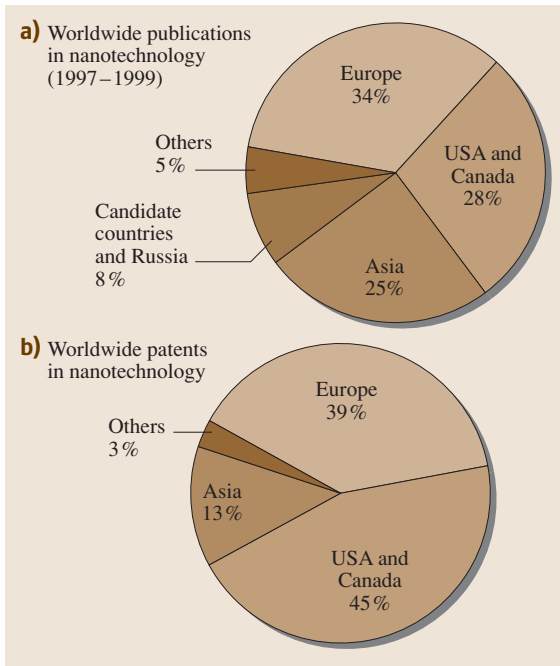


Fig. 1.5a,b Breakdown of (a) worldwide publications and (b) worldwide patents (source: European Commission 2003)

December 3, 2003, President George W. Bush signed into law the 21st Century Nanotechnology Research and Development Act. The legislation put into law programs and activities supported by the National Nanotechnology Initiative. The bill gave nanotechnology a permanent home in the federal government and authorized \$3.7 billion to be spent in the 4-year period beginning in October 2005 on nanotechnology initiatives at five federal agencies. The funds would provide grants to researchers, coordinate R&D across five federal agencies [National Science Foundation (NSF), Department of Energy (DOE), NASA, National Institute of Standards and Technology (NIST), and Environmental Protection Agency (EPA)], establish interdisciplinary research centers, and accelerate technology transfer into the private sector. In addition, the departments of Defense (DOD), Homeland Security, Agriculture, and Justice, as well as the National Institutes of Health (NIH), also fund large R&D activities. They currently account for more than one third of the federal nanotechnology budget.

The European Union (EU) made nanosciences and nanotechnologies a priority in the Sixth Framework Program (FP6) in 2002 for the period 2003–2006. They had dedicated modest funds in FP4 and FP5. FP6 was

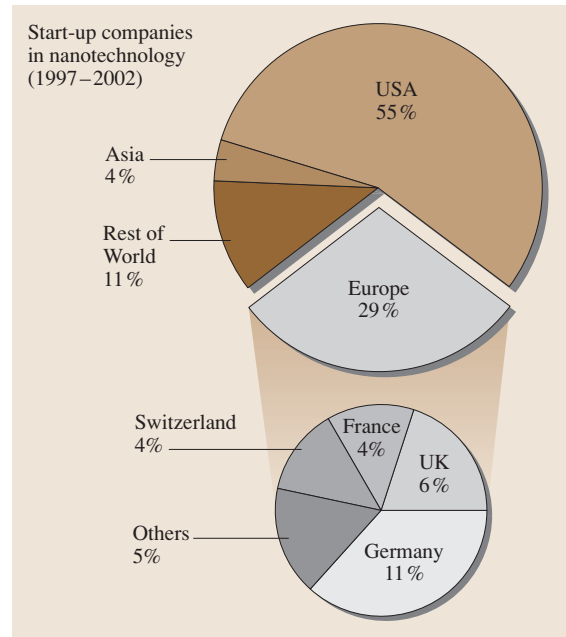


Fig. 1.6 Breakdown of startup companies around the world (1997–2002) (source: CEA, Bureau d’Etude Marketing)

tailored to better help structure European research and to cope with the strategic objectives set out in Lisbon in 2000. Japan identified nanotechnology as one of its main research priorities in 2001. The funding levels increased sharply from \$400 million in 2001 to around \$950 million in 2004. In 2003, South Korea embarked on a 10-year program with around \$2 billion of public funding, and Taiwan has committed around \$600 million of public funding over 6 years. Singapore and China are also investing on a large scale. Russia is well funded as well.

Figure 1.3a shows the public expenditure breakdown in nanotechnology R&D around the world, with about US\$5 billion in 2004, being about equal by USA, Japan, and Europe. Next we compare public expenditure on a per-capita basis. The average expenditures per capita for the US, EU-25, and Japan were about \$3.7, \$2.4, and \$6.2, respectively [1.11]. Figure 1.3b shows the breakdown of expenditures in 2004 by public and private sources with more than \$10 billion spent on nanotechnology research. Two thirds of this came from corporate and private funding. The private expenditure in the United States and Japan was slightly larger than that of the public, whereas in Europe it was about one third. Figure 1.4 shows the public and private expenditure breakdown in 2004 in various countries. Japan

and the US had the largest expenditure, followed by Germany, Taiwan, South Korea, UK, Australia, China, France, and Italy. Figure 1.5 shows the breakdown of worldwide publications and patents. The US and Canada

led, followed by Europe and Asia. Figure 1.6 shows the breakdown in startup companies around the world (1997–2002). Entrepreneurship in the USA is clearly evident followed by Europe.

1.3 Lessons from Nature (Biomimetics)

Nanotechnology is a new word, but it is not an entirely new field. Nature has many objects and processes that function on a micro- to nanoscale [1.9, 12]. The understanding of these functions can guide us to imitate and produce nanodevices and nanomaterials. Abstractions of good design from nature are referred to as biomimetics.

Billions of years ago, molecules began organizing into the complex structures that could support life. Photosynthesis harnesses solar energy to support plant life. Molecular ensembles present in plants, which include light-harvesting molecules such as chlorophyll arranged within the cells on the nanometer to micrometer scales, capture light energy and convert it into the chemical energy that drives the biochemical machinery of plant cells. Live organs use chemical energy in the body. The flagellum, a type of bacteria, rotates at over 10 000 RPM [1.13]. This is an example of a biological molecular machine. The flagellum motor is driven by the proton flow caused by the electrochemical potential differences across the membrane. The diameter of the bearing is about 20–30 nm with an estimated clearance of about 1 nm.

In the context of tribology, some biological systems have antiadhesion surfaces. First, many plant leaves (such as the lotus leaf) are covered by a hydrophobic cuticle, which is composed of a mixture of large hydrocarbon molecules that have a strong aversion to water. Second, the surface has a unique roughness distribution [1.14, 15]. It has been reported that for some leaf surfaces, the roughness of the hydrophobic leaf surface decreases wettability, which is reflected in a greater contact angle of water droplets on such surfaces.

“Geckos” (a family of lizards) are known for their amazing climbing ability. They can run up any wall, run across the ceiling, and stick to ceilings. They rely on the extreme miniaturization and multiplication of contact elements. Soles of geckos are covered with about half a million submicrometer keratin hairs, called spatulae, which are what make their feet, known as “gecko feet”,

so sticky. Each hair is 30–130 μm long and is only one tenth the diameter of a human hair and contains hundreds of projections terminating in 0.2–0.5 μm spatula-shaped structures. The foot typically has about 5000 hair/ mm^2 . Each hair produces a tiny force (≈ 100 nN), primarily due to van der Waals attraction, and possibly capillary interactions (meniscus contribution), and millions of hairs acting together create a large adhesive force on the order of 10 N with a pad area of approximately 100 mm^2 [1.16], sufficient to keep geckos firmly on their feet, even when upside down on a glass ceiling. The bonds between hair and a surface can be easily broken by “peeling,” in the same way one removes a strip of adhesive tape, allowing geckos to run across ceilings.

Spiders, a family of arthropods (spiders, insects, and crustaceans) can stick to smooth, overhanging surfaces also because of a large number of hairs and the microstructure of the hairs on their feet. Spiders use claws to attach to rough surfaces but have scopulae (tufts of hairs) on their feet to adhere to smooth surfaces. The scopulae hairs of the jumping spider, *Evarcha arcuata*, branch into a very large number of smaller hairs or setulae, whose broadened ends have a contact area of about 2×10^5 nm^2 [1.17]. The number of setulae per foot is about 80, 000 giving a total of about 700, 000 contact points for the spider’s eight legs [1.17]. This provides a large amount of adhesive force because of van der Waals attraction added on all legs. The hair surface (cuticle) is sealed with a topographically microconfigured wax layer. These surfaces are reportedly nonwetable, so capillary interactions are not expected to be significant.

Scientists are attempting to create a new type of adhesive tape by mimicking the structure of gecko or spider feet. Geim et al. [1.18] reported the fabrication of a “gecko” tape made by microfabrication of dense arrays of flexible plastic pillars that are little more than 2 μm tall with a pitch on a similar scale.

1.4 Applications in Different Fields

Science and technology continue to move forward in making the fabrication of micro/nanodevices and systems possible for a variety of industrial, consumer, and biomedical applications (see, e.g., [1.19, 20]). A variety of MEMS devices have been produced, and some are commercially used [1.12, 21–29]. Several types of sensors are used in industrial, consumer, defense, and biomedical applications. Various micro/nanostructures or micro/nanocomponents are used in microinstruments and other industrial applications such as micromirror arrays. The largest “killer” MEMS applications include accelerometers (some 90 million units installed in vehicles in 2004), silicon-based piezoresistive pressure sensors for manifold absolute pressure sensing for engines and for disposable blood pressure sensors (about 30 million units and about 25 million units, respectively), capacitive pressure sensors for tire pressure measurements (about 37 million units in 2005), thermal inkjet printheads (about 500 million units in 2004), and digital micromirror arrays (about \$700 million in revenue in 2004). Other applications of MEMS devices include chemical/biosensors and gas sensors, microresonators, infrared detectors, and focal plane arrays for earth observations, space science, and missile defense applications, picosatellites for space applications, fuel cells, and many hydraulic, pneumatic, and other consumer products. MEMS devices are also being explored for use in magnetic storage systems (*Bhushan* [1.30]), where they are being developed for supercompact and ultrahigh-recording-density magnetic disk drives.

NEMS are produced by nanomachining in a typical top-down and bottom-up approach, largely relying on nanochemistry [1.31–37]. Examples of NEMS include microcantilevers with integrated sharp nanotips for scanning tunneling microscopy (STM) and atomic force microscopy (AFM), quantum corral formed using STM by placing atoms one by one, AFM cantilever array (Millipede) for data storage, AFM tips for nanolithography, dip-pen lithography for printing molecules, nanowires, carbon nanotubes, quantum wires, quantum boxes, quantum-dot transistors, nanotube-based sensors, biological (DNA) motors, molecular gears by attaching benzene molecules to the outer walls of carbon nanotubes, devices incorporating nanometer-thick films (e.g., in giant magnetoresistive or GMR read/write magnetic heads and magnetic media) for magnetic rigid disk drives and magnetic tape drives, nanopatterned magnetic rigid disks, and nanoparticles (e.g., nanoparticles in magnetic

tape substrates and magnetic particles in magnetic tape coatings).

Nanoelectronics can be used to build computer memory using individual molecules or nanotubes to store bits of information, molecular switches, molecular or nanotube transistors, nanotube flat-panel displays, nanotube integrated circuits, fast logic gates, switches, nanoscopic lasers, and nanotubes as electrodes in fuel cells.

BioMEMS/BioNEMS are increasingly used in commercial and defense applications; see, e.g., [1.38–44]. They are used for chemical and biochemical analyses (biosensors) in medical diagnostics (e.g., DNA, RNA, proteins, cells, blood pressure and assays, and toxin identification) [1.44, 45], tissue engineering [1.46], and implantable pharmaceutical drug delivery [1.47, 48]. Biosensors, also referred to as biochips, deal with liquids and gases. There are two types. A large variety of biosensors are based on micro/nanofluidics. Micro/nanofluidic devices offer the ability to work with smaller reagent volumes and shorter reaction times, and perform analyses multiple times at once. The second type of biosensors includes micro/nanoarrays that perform one type of analysis thousands of times. Micro/nanoarrays are a tool used in biotechnology research to analyze DNA or proteins to diagnose diseases or discover new drugs. Also called DNA arrays, they can identify thousands of genes simultaneously [1.41]. They include a microarray of silicon nanowires, roughly a few nanometers in size, to selectively bind and detect even a single biological molecule, such as DNA or protein, using nanoelectronics to detect the slight electrical charge caused by such binding, or a microarray of carbon nanotubes to electrically detect glucose.

After the tragedy of September 11, 2001, concern over biological and chemical warfare has led to the development of handheld units with bio- and chemical sensors for the detection of biological germs, chemical or nerve agents, and mustard agents and to chemical precursors to protect subways, airports, water supply, and the population at large [1.49].

BioMEMS/BioNEMS are also being developed for minimal invasive surgery including endoscopic surgery, laser angioplasty, and microscopic surgery. Other applications include implantable drug-delivery devices—micro/nanoparticles with drug molecules encapsulated in functionalized shells for site-specific targeting applications and a silicon capsule with a nanoporous membrane filled with drugs for long-term delivery.

1.5 Various Issues

There is an increasing need for a multidisciplinary, system-oriented approach to the manufacture of micro/nanodevices that function reliably. This can only be achieved through the cross-fertilization of ideas from different disciplines and the systematic flow of information and people among research groups. Common potential failure mechanisms for MEMS/NEMS requiring relative motion that need to be addressed in order to increase their reliability are adhesion, friction, wear, fracture, fatigue, and contamination [1.50–53]. Surface micro/nanomachined structures often include smooth and chemically active surfaces. Due to a large surface area to volume ratio in MEMS/NEMS, they are particularly prone to stiction (high static friction) as part of normal operation. Fracture occurs when the load on a microdevice is greater than the strength of the material. Fracture is a serious reliability concern, particularly for brittle materials used in the construction of these components, since it can immediately or would eventually lead to catastrophic failures. Additionally, debris can be formed from the fracturing of microstructures, leading to other failure processes. For less brittle materials, repeated loading over a long period of time causes fatigue that would also lead to the breaking and fracturing of the device. In principle, this failure mode is relatively easy to observe and simple to predict. However, the material properties of thin films are often not known, making fatigue predictions error prone.

Many MEMS/NEMS devices operate near their thermal dissipation limit. They may encounter hot spots that may cause failures, particularly in weak structures, such as diaphragms or cantilevers. Thermal stressing and relaxation caused by thermal variations can create material delamination and fatigue in cantilevers. In large temperature changes, as experienced in outer space, bimetallic beams will also experience warping due to mismatched coefficients of thermal expansion. Packaging has been a big problem. The contamination, which probably happens in packaging and during storage, also can strongly influence the reliability of MEMS/NEMS. For example,

a particulate dust that lands on one of the electrodes of a comb drive can cause catastrophic failure. There are no MEMS/NEMS fabrication standards, which makes it difficult to transfer fabrication steps in MEMS/NEMS between foundries.

Obviously, studies of determination and suppression of active failure mechanisms affecting this new and promising technology are critical to a high reliability of MEMS/NEMS and are determining factors in successful practical application.

Adhesion between a biological molecular layer and the substrate, referred to as “bioadhesion,” and reduction of friction and wear of biological layers, biocompatibility, and biofouling for BioMEMS/BioNEMS are important.

Mechanical properties are known to exhibit a dependence on specimen size. Mechanical property evaluation of nanometer-scaled structures is carried out to help design reliable systems since good mechanical properties are of critical importance in such applications. Some of the properties of interest are Young’s modulus of elasticity, hardness, bending strength, fracture toughness, and fatigue life. Finite element modeling is carried out to study the effects of surface roughness and scratches on stresses in nanostructures. When nanostructures are smaller than a fundamental physical length scale, conventional theory may no longer apply, and new phenomena emerge. Molecular mechanics is used to simulate the behavior of a nanoobject.

The societal, ethical, political, and health/safety implications are receiving considerable attention [1.11]. One of the prime reasons is to avoid some of the public skepticism that surrounded the debate over biotech advances such as genetically modified foods, while at the same time dispelling some of the misconceptions the public may already have about nanotechnology. Health/safety issues need to be addressed as well. For example, one key question is what happens to nanoparticles (such as buckyballs or nanotubes) in the environment and whether they are toxic in the human body if ingested.

1.6 Research Training

With a decreasing number of people in western countries going into science and engineering and with the rapid progress being made in nanoscience and nanotechnology, the problem of a trained work force is expected to be acute. Education and training is essential

to produce a new generation of scientists, engineers, and skilled workers with the flexible and interdisciplinary R&D approach necessary for rapid progress in nanosciences and nanotechnology [1.54]. The question is being asked: Is the traditional separation of

academic disciplines into physics, chemistry, biology, and various engineering disciplines meaningful at the nano level? Generic skills and entrepreneurship are needed to translate scientific knowledge into products. Scientists and engineers in cooperation with relevant experts should address the societal, ethical, political, and health/safety implications of their work for society at large.

To increase the pool of students interested in science and technology, science needs to be projected as exciting at the high school level. Interdisciplinary curricula relevant for nanoscience and nanotechnology need to be developed. This requires revamping the education, developing new courses and course materials including textbooks [1.28, 36, 53, 55–57] and instruction manuals, and training new instructors.

1.7 Organization of Handbook

The handbook integrates knowledge from the point of view of fabrication, mechanics, materials science, and reliability. Organization of the book is straightforward. The handbook is divided into eight parts. The first part of the book includes an introduction to nanostructures, micro/nanofabrication, methods, and materials. The second part introduces various MEMS/NEMS and BioMEMS/BioNEMS devices. The third part introduces scanning probe microscopy. The fourth part provides an

overview of nanotribology and nanomechanics, which will prepare the reader for understanding the tribology and mechanics of industrial applications. The fifth part provides an overview of molecularly thick films for lubrication. The sixth part focuses on industrial applications, and the seventh part focuses on microdevice reliability. Finally, the last part focuses on technological convergence from the nanoscale as well as the social, ethical, and political implications of nanotechnology.

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