Introduction to Nanotechnology

Risal Singh
Former Scientist
Solid State Physics Laboratory (DRDO), Delhi

Shipra Mital Gupta
Assistant Professor
University School of Basic and Applied Sciences,
Guru Gobind Singh Indraprastha University, Delhi

OXFORD
UNIVERSITY PRESS

OXFORD
UNIVERSITY PRESS

Oxford University Press is a department of the University of Oxford.
It furthers the University's objective of excellence in research, scholarship, and education by publishing worldwide. Oxford is a registered trade mark of Oxford University Press in the UK and in certain other countries.

Published in India by
Oxford University Press
YMCA Library Building, 1 Jai Singh Road, New Delhi 110001, India

First published in 2016

ISBN-13: 978-0-19-945678-9
ISBN-10: 0-19-945678-X

Typeset in Times
by QuADS Prepress Private Limited, Chennai
Printed in India by Magic International (P) Ltd, Greater Noida

Dedicated to the memory of
My beloved parents
Khajano Devi and Chhidda Singh
and elder sister
Kashmere Devi

Risal Singh

Dedicated to my
grandparents, *parents*, *in-laws*, and *husband*

Shipra Mital Gupta

Preface

Nanotechnology is the science and technology of manipulating matter at the atomic or molecular scale, thereby creating endless possibilities towards realizing improved devices, structures, and materials with dimensions in the range of 1–100 nanometres. Being heralded as a new technological revolution, nanotechnology has evolved in the later part of the 20th century as a product of the drive towards miniaturization led by semiconductor technology. It has emerged as one of the most exciting and sought after fields due to its technological and strategic importance as it embraces all branches of science and engineering, influencing every walk of our lives—from the food we eat to the clothes we wear, the medicines we use, the buildings we live in, the electronic appliances we use, and all other spheres of life one can think of.

It is emphasized at the very beginning of the book that the development of nanoscience and nanotechnology, as envisaged by Richard Feynman, could be realized only due to the great advances in very large scale integration (VLSI) technology after the invention of the transistor in 1947 and the advancements in the fields of electron microscopy and crystallography that lead to the development of sophisticated tools such as scanning tunnelling microscopy and atomic force microscopy, which have enabled the handling of individual atoms and molecules and imaging with a resolution at the atomic scale.

The motive behind writing this book was to percolate the knowledge of this fast-growing technology to a wide cross-section of students of all disciplines of science and engineering in a sufficiently thorough and comprehensible format, so as to facilitate an insight into the field. Not only students, this book will reach out to all individuals who are keen to know about the working of nature and other vast prospects of the field of nanotechnology.

Paramount importance has been placed in the book on the understanding of nanostructures in the form of low-dimensional quantum dots, wires and tubes, and their applications in quantum electronics. Topics have been carefully selected to emphasize the understanding of nanodevices and nanomachines in their role as substitutes to their conventional electrical, electronic, and mechanical analogues.

ABOUT THE BOOK

This book has been written to suit a typical one-semester interdisciplinary course on the subject offered to the undergraduate science and engineering students of all Indian universities. It will also be useful for various postgraduate programmes offering a similar course. It is aimed at providing not only an overview of nanotechnology, but also imparting an understanding of the ultimate scale of molecules and tiny atomic clusters, including fabrication of nanostructures and devices. The reader is presumed to have knowledge of basic sciences at the seniorsecondary level in order to understand the material provided in this book. The mathematical aspect of this subject is kept to a bare minimum and numerical exercises can be solved based on the formulae and equations provided in the chapters. Moreover, answers to these exercises are provided at the end of each chapter. We have attempted to introduce the subject in a manner that enables even researchers from other fields to obtain an overview of the recent developments in this exciting field.

KEY FEATURES

- Provides an introduction to the basic concepts of nanotechnology
- Discusses in detail advanced topics such as quantum nanoelectronics and nanoelectromechanical systems (NEMS)
- Includes carefully written chapter summaries to assist in quick recapitulation and a comprehensive glossary for reference
- Includes an *exercises* section with review questions, multiple-choice questions (MCQs), fill in the blanks, match the following, etc., at the end of each chapter

ONLINE RESOURCES

The following resource is available at the online resources centre for faculty and students using this text:

- PowerPoint presentations modularized according to the chapters

CONTENT AND STRUCTURE

The chapters of this book are divided into five parts. Part I deals with the introduction to nanotechnology. Part II includes three chapters on physics applied to nanostructures, covering basic concepts that help in preparing the students to understand the concepts behind nanotechnology. Part III describes nanomaterials and devices, comprising of seven chapters that form the main body of the book. Part IV deals with the practical aspects of nanomaterial growth, synthesis, and characterization techniques. Part V includes chapters on the applications and societal impact of nanotechnology.

Part I Introduction

Chapter 1 traces the evolution of the field of nanotechnology, covering the epoch of great discoveries. It defines the physical size scales of the objects in relation to the nanoscale, describes Richard Feynman's great vision of the small world, Eric Drexler's nanoscale assembler, and nature's working at the molecular level. It also deals with the existence of nanostructures in nature and the use of nanomaterials prior to the nano-era and explains why nanoparticles behave differently as compared to macro- and micro- objects.

Part II Physics Applied to Nanostructures

Chapters 2, *3*, and *4* describe the physics background of crystal structures, principles of quantum mechanics, and the energy-band concepts essential for assimilating concepts of nanotechnology and understanding the properties of nanomaterials and device characteristics. *Chapter 2* describes size dependency of material properties, crystal structures, X-ray, electron, and neutron wave diffraction by crystals, etc., with the description of X-ray diffraction methods, electron microscopy and crystallography, lattice vibrations, and crystal structure of nanomaterials. *Chapter 3* deals with quantum mechanics as applied to nanostructures of quantum dots, quantum wires, and quantum wells. *Chapter 4* explains the basics of energy bands, including the electronic structure of nanoparticles.

Part III Nanomaterials and Devices

Chapters 5, *6*, and *7* present the physical structures and properties of nanoclusters, nanotubes, and other nanostructures. *Chapter 5* deals specifically in carbon nanoclusters and describes the synthesis and properties of graphene, fullerenes, nanodiamonds, and diamond-like carbon structures. *Chapter 6* describes the carbon nanotubes (CNTs)—their structure, growth and purification mechanisms, physical (electrical, electronic, optical, vibrational, and mechanical) and chemical properties, and toxicity, along with a summary on some inorganic nanotubes. *Chapter 7* further elucidates on structural and physical properties, including structural, electronic, magnetic, electrical, optical, and mechanical properties.

Chapter 8 on nanoferromagnetism describes the synthesis of magnetic nanoparticles, tailoring of magnetization characteristics of nanostructured bulk magnetic materials, Stoner–Wohlfarth model for dynamic behaviour of nanomagnetic grains, carbon nanoferromagnets, inorganic ferromagnetic nanoparticles, magneto-resistance effect, and ferrofluids.

Chapters 9 and *10* discuss quantum electronic devices, nanomachines, and nanodevices. *Chapter 9* discusses resonant tunnel diodes, single electron devices, quantum cascade and quantum dot lasers, quantum well infrared photodetectors, Josephson junction and its application in superconducting quantum interference device, and photonic crystal. *Chapter 10* introduces microelectromechanical systems (MEMS)—a precursor to nanoelectromechanical systems (NEMS), nanomachines, and devices. It also explains MEMS fabrication by bulk and surface micromachining, with MEMS accelerometer as an example, NEMS characteristics and technology-related challenges, molecular switches and machines, and quantum computing machine.

Chapter 11 presents nanomaterials and biosystems, describing biological nanomaterials, such as magnetosomes, spider silk, bone, and abalone shell, and the synthesis of bionanomaterials by biomimetic methods. It also discusses nanocircuitry, bioelectronic, nanomechanical, and computational devices, bionanosensors, molecular imaging, and targeted drug delivery.

Part IV Nanomaterial Growth and Characterization

Chapters 12 and *13* discuss the methods of growth and synthesis of nanomaterials and their characterization. *Chapter 12* presents top-down and bottom-up approaches to nanostructure fabrication, photolithographic techniques, vacuum systems, physical and chemical deposition, epitaxial growth methods of nanofilms, and scanning probe and other deposition/growth methods of nanostructures. It further discusses the chemical methods of synthesis, such as co-precipitation, sol–gel, microemulsion, solvothermal, microwave, sonochemical, radiation-assisted, and biological synthesis, including those using microorganisms, biological templates, and plant extracts**.** *Chapter 13* delves on characterization tools and methods for particle size, composition, and surface structure determination of nanomaterials using electron diffraction, electron microscopy, and spectroscopic techniques.

Part V Applications and Societal Impact

In conclusion, *Chapters 14* and *15* describe the applications and societal impact of nanotechnology.

Chapter 14 includes applications of nanotechnology in the following areas.

1. Energy, such as solar photovoltaics and thermal collectors, fuel cells, energy storage, power generation and distribution, and energy saving materials and devices
2. Information technology, such as displays and computers
3. Defence
4. Medicine and consumer goods

Chapter 15 presents the societal implications of nanotechnology, issues related to health, environment, energy, water and food, and other aspects of nanotechnology, such as toxicity monitoring, risk management, protocols and regulations, nanoethics, public perception, and future perspectives.

Appendices A and *B* list the physical constants and the properties of important semiconductors, respectively.

Readers are welcome to share feedback and suggestions for further improvement of the book with the authors at risal_singh@yahoo.co.in and shipra.mital@gmail.com.

Risal Singh
Shipra Mital Gupta

Acknowledgements

I am indebted to Dr R. Muralidharan (former Director), Dr R.K. Sharma (Director), Dr A.K. Kapoor (Associate Director), and Dr Anshu Goyal (Scientist 'E') of Solid State Physics Laboratory, SSPL, Delhi for granting permission to include some of the figures of their X-ray diffraction work in this book.

I extend my heartfelt thanks to several colleagues and friends from SSPL, Delhi, especially Anil K. Gupta, Dr P.K. Chaudhury, Dr R.K. Bhan, Dr N.D. Arora, Dr R.S. Saxena, Bharatvir Singh, and Kailash Sharma for their constant support and inspirational discussions. Thanks are also due to Prof. S.B. Bajpayee (Dean, Academics) and Rupesh Rana from KEC, Ghaziabad for their encouragement and support.

I express my gratitude to the management and the editorial team at Oxford University Press, India for their continuous guidance, encouragement, and support in bringing out this book, all of which was of immense help in realizing the book in its present form.

Last but not the least, I thank my wife Pushpa, daughter Shailja and her husband Mukesh Roy, and son Vivek and his wife Poonam for their continuous support and encouragement and my elder brothers Jaswant and Bhagwant for their blessings.

Risal Singh

I express my gratitude to the honorable Vice Chancellor, Guru Gobind Singh Indraprastha University (GGSIPU), Delhi and Dean, University School of Basic and Applied Studies (USBAS), Delhi for their professional guidance and encouragement, which has been a source of strength. Innumerable thanks are extended to colleagues from USBAS and also other colleagues at GGSIPU, who have been constantly supportive. Thanks are also due to the supporting staff of GGSIPU for their cooperation. Sincere acknowledgements are due to Prof. Anil Kumar, Indian Institute of Technology Roorkee for his encouragement and valuable support.

I thank my *baba*, *dadi*, *nani*, and *nana* for being my true inspiration. I am thankful to my parents-in-law and parents for their blessings. I extend my special thanks to sister Mukta for her continuous encouragement. Finally, very special thanks to my soul-mate and companion Anil for bearing the most.

Shipra Mital Gupta

Features of the Book

Learning Objectives

After going through this chapter, the reader will be ab

- trace the origin of nanoscience and technology

Learning Objectives
Briefs about all the topics discussed in the chapter

Figures and Images
Numerous well-illustrated figures and images provide for better understanding of concepts

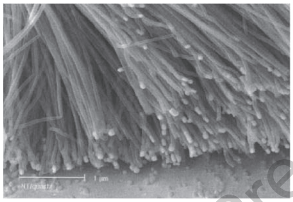
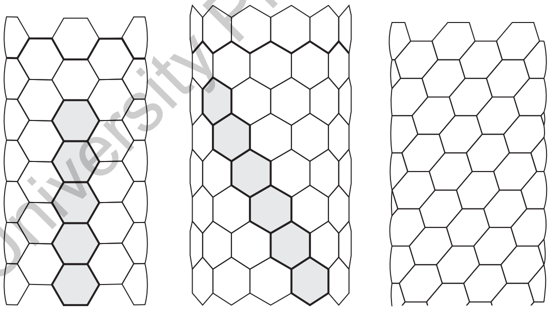


FIG. 8.7 SEM image of the iron particles on the tips of the aligned nanotubes

Courtesy: Reprinted from *Journal of Magnetism and Magnetic Materials*, **231**, 'Magnetic Properties of Fe Nanoparticles Trapped at the Tips of the Aligned Carbon Nanotubes', Page No. 9–12, Copyright 2001, with permission from Elsevier.



(a) (b) (c)

FIG. 6.5 Types of carbon nanotubes (a) Armchair (b) Zigzag (c) Chiral

Max von Laue (1879–1960)

In 1905, Max von Laue joined Max Planck Institute for Theoret thermodynamic aspects of the coherence of light waves.

Paul Ewald, who gave a first theoretical explanation of th in crystals in his doctoral thesis supervised by Arnold Somm

Biographies
Describe prominent scientists who have made significant contributions in the field of nanoscience

Summary
Enables the recapitulation of important concepts discussed in the chapter

SUMMARY

- The properties of bulk material particles are ind properties of nanoparticles are dependent on their s nanoparticles is large compared to the number of at properties are, therefore, greatly influenced by thei

KEY TERMS

Eigen energy/Eigen value Solution of the Schrödinger equation, when applied to a quantum system such as atoms, molecules, and nanoparticles, yields discrete energy values called *eigen energy* values or *eigen values* for box and degree (one or r which a nanosca

Key Terms
Enable students to recollect concepts related to physical and chemical sciences learnt in higher secondary classes

EXERCISES

REVIEW QUESTIONS

4.1 Differentiate between the direct and indirect band se

MULTIPLE-CHOICE QUESTIONS

4.1 Who postulated the particle–wave duality principle'
(a) Albert Einstein (b) Niels Bohr

FILL IN THE BLANKS

4.1 The semi-classical free electron theory using Ferr

MATCH THE FOLLOWING

5.1 Graphite (a) 3D struct
5.2 Diamond (b) Fullerene

STATE WHETHER TRUE OR FALSE

9.1 QCLs are based on interband transitions.

Exercises
Sections such as review questions, multiple choice questions, fill in the blanks, match the following, and state whether true or false test the understanding of the concepts discussed

NUMERICAL PROBLEMS

9.1 Calculate the value of tunnel resistance so that the (than the Heisenberg's energy uncertainty. [*Hint* Δt constant of the tunnel junction resistance circuit. Ap
9.2 Calculate the minimum charging voltage for a singl

Numerical Problems
Included along with answers, in relevant chapters

References
Included in each chapter for those who wish to gather some additional information on certain topics

REFERENCES

Agnihotri, M., Joshi, S., Kumar, A.R., Zinjarde, S., and I Nanoparticles by the Tropical Marine Yeast Yarrowia Vol. **63**, pp. 1231–1234 (2009).

Companion Online Resources

Visit india.oup.com/orcs/9780199456789 to access teaching and learning solutions online.

The following resources are available to support the faculty and students using this book:

- PowerPoint presentations

Steps to register and access Online Resources

Resources for instructors and students are developed to complement each textbook and vary from book to book.

Step 1: Getting Started

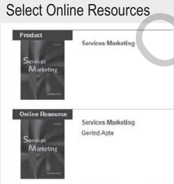
- Go to india.oup.com

Step 2: Browse quickly by:

- BASIC SEARCH
  - AUTHOR
  - TITLE
  - ISBN
- ADVANCED SEARCH
  - KEYWORDS
  - AUTHOR
  - TITLE
  - SUBTITLE
  - PUBLICATION DATE

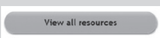
Step 3: Select Title

- Select Product
- Select Online Resources



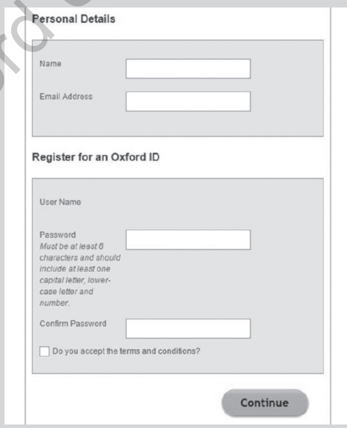
Step 4: View Resources

- Click on “View all resources”



Step 5: Sign in with your Oxford ID

Step 6: If you do not have an Oxford ID, register with us



Step 7: Fill in your details

- Fill the detailed registration form with correct particulars.
- Fields marked with ‘*’ in the form are mandatory.
- Update

Step 8: Validation

- We shall revert to you within 48 hours after verifying the details provided by you. Once validated, please login using your username and password and access the resources.

Step 9: Confirmation

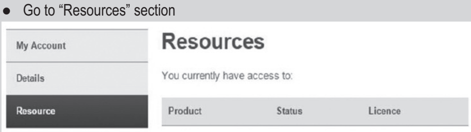
- You will receive a confirmation on your email ID.

Step 10: Visit us again

- Go to india.oup.com
- Sign in with Oxford ID

Step 11: Visit your licensed products

- Go to “Resources” section



Step 12: Download Resources

- Click on the title
- View online resources
- Select resource type
- Download the resource you require

For any further queries, please write to us at HEMarketing.in@oup.com with your mobile number.

Brief Contents

Detailed Contents

NANOTECHNOLOGY—AN INTRODUCTION

1

Learning Objectives

After going through this chapter, the reader will be able to

- trace the origin of nanoscience and technology
- learn about the efforts taken towards miniaturization of devices and systems, particularly in the fields of integrated circuits and computer technology that prepared the ground to embark upon research and development programmes in science and technology of the small world
- have a glimpse of Richard Feynman's 'big vision of the small world'
- learn about the advances in the field of imaging technologies such as optical, electron, and atomic force microscopy, NMR imaging (MRI), and X-ray and electron diffraction methods in determination of the physical and electronic structures of atomic clusters/nanostructures, setting the stage for the arrival of nanotechnology in the 1980s
- understand the important role played by the development of scanning probe microscopes—particularly the use of scanning tunneling microscopes—in providing atom-by-atom handling capability in the assembly of nanostructures and devices
- learn about the position of nanometre scale (nanoscale) in the scheme of different scales and form an idea about the relative size of nanosize objects
- appreciate the multidisciplinary nature of nanotechnology that embraces all the branches of science and technology
- know that the properties of nanoscale particles and structures show dependence on size and dimensions, with high surface-to-volume ratio
- realize that quantum mechanics is the key to understanding the behaviour of nanosize structures, devices, and machines
- learn about the existence of nanostructures in nature, both living and non-living
- know that nanomaterials were already in use for ages
- have a glimpse of the prospects of nanotechnology

1.1 INTRODUCTION

The word 'nano' is derived from the Greek word *nanos* or Latin word *nanus*, meaning 'dwarf'. It qualifies objects of matter having at least one physical dimension in the range 1–100 nanometres, as nanoscale objects. Here, one nanometre, abbreviated as nm, refers to a billionth of a metre, that is, 10^{-9} metre. Such nanoscale objects of matter are referred to as nanoparticles, nanomaterials, or nanostructures. The branch of science dealing with the systematic study of nature and behaviour of nanomaterials based on experimental observations and formulation of general laws describing their properties is called *nanoscience*. Norio Taniguchi, professor at Tokyo University, coined the term *nanotechnology* for the first time in 1974 to describe semiconductor processes such as thin-film deposition and ion-beam milling exhibiting characteristic control on the order of a nanometre. Nanotechnology cuts across all disciplines, borrowing liberally from physics, chemistry, material science, and biology, and is truly multidisciplinary in nature, as shown in Fig. 1.1. Based on the fundamental research and understanding of nanomaterials, nanotechnology enables development of products with possible practical applications employing nanostructures.

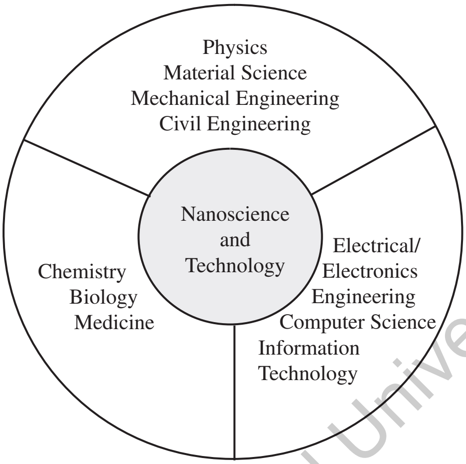


FIG. 1.1 Various disciplines engaged in research and development in nanotechnology

Scientists and technologists have always been fascinated and are working tirelessly to make novel and improved devices as a symbol of the continuous progress of mankind, in terms of their size, performance, and cost. To achieve this goal, they have laid major emphasis on the miniaturization of the devices and implements, which has been particularly useful in the field of electronics. The bulky vacuum tubes were replaced by discrete semiconductor junction transistors, which in turn, gave way to integrated circuits. The bipolar integrated circuits have been substituted by low power, economic, metal-oxide semiconductor (MOS) technology. Then, microelectromechanical systems (MEMS), with devices and machines on the micron to millimetre scale, were developed in the last three decades. In a quick succession to MEMS technology, nanotechnology has opened new avenues for fabrication of devices and systems on the nanoscale with high sensitivity and frequency response in the range of gigahertz and beyond.

1.2 HISTORICAL PERSPECTIVES

The emergence of nanotechnology is based on the fundamentals of quantum mechanics and other scientific and technological advances in the last hundred years or more. Even today, microwave vacuum tubes form a part of the high frequency communication systems such as mobile phones, Wi-Fi, radar, and satellite transmission. This era has provided sophisticated tools and techniques for investigating the atomic structure of solids such as X-ray, electron, and neutron crystallography and imaging techniques such as scanning probe electron and atomic force microscopes, making it possible to image down to the atomic level. These tools and techniques form the basic necessity for imaging and characterization of nanostructures and devices. They are discussed in the following sections.

1.2.1 Vacuum Electron Tube

Developments in the field of electronics beginning from the late 19th century have played the most dominant role in the rapid progress of science and technology. The invention of the vacuum tube, an active component of electronic circuits, was crucial to the initial growth of electronics and was the first major landmark in the history of electronics. The vacuum tube, consisting of two or more electrodes vacuum-sealed in a thin transparent glass or metal–ceramic container, is essentially based on thermionic emission of electrons, and is used in electronic circuits to control the flow of electrons between electrodes.

The thermionic emission, later used in making vacuum tubes, was first observed by Frederick Guthrie in 1873. He observed that the negatively charged red-hot iron sphere was getting discharged, but the same effect did not happen if the sphere was positively charged. Thomas Edison took the next step in 1883 while developing the incandescent electric bulb. He faced the problem of the glass casing of the electric bulbs becoming blackened, making their lives short. It was known to him that the particles leaving the hot element were negatively charged, which on striking the glass caused blackening. He, therefore, introduced a second element with positive polarity to attract the negative particles to get rid of the problem and observed the flow of current between the hot element and the positive electrode in the circuit. However, on reversing the potentials, he noticed that this did not happen. Though fascinated by the effect, Edison could not make any practical use of the effect and it was later termed as the *Edison effect*. Subsequent to identification of the electron by J.J. Thomson, Owen W. Richardson further studied the phenomenon of electron ejection from red-hot metals, terming it the *thermionic emission*, thus formulating the law of thermionic emission in 1901.

John A. Fleming was the first to transform the observation of the Edison effect into a practical device in 1901. By then it was known that the charged particles emitted by the hot filament were electrons, which were attracted by positive electrodes. Fleming observed that when an alternating current with frequency 80–100 Hz was passed through the bulb, only half cycle was passed, that is, it was rectified producing direct current. He called the device *oscillating valve* in analogy to the valve in a pump that allows water or gas to flow only in one direction. This was the first electronic rectifier diode and was known as *Fleming valve*. The device was intended for application in detecting spark-generated radio waves in communication. In 1907, Lee de Forest advanced the vacuum tube technology further by introducing a third electrode in the Fleming diode called *grid* that controlled the current in the tube, forming a triode electron tube called *Audion*. He further improved upon Audion and successfully demonstrated its use as an amplifier in 1911, thereby effectuating a revolution in electronics.

Walter Schottky, while studying under Max Planck in Berlin in 1914, discovered the random noise in vacuum tubes called *shot noise*, which was caused by the statistical nature of the thermionic emission of electrons by the cathode and their irregular arrival at the anode. He invented the first multiple grid vacuum tube in 1919 called *tetrode* with four electrodes, by introducing a second grid called the *screen grid* between the control grid and the anode to act as an electrical screen or a shield. This innovative modification in the triode decouples the anode and the control grid, basically eliminating the problems associated with *Miller effect*, which refers to the dependence of the effective input impedance of an amplifier on the impedance connected from input to output of the amplifier. However, performance of the tetrode was affected by the secondary emission of electrons at the anode, which could outnumber the primary electrons, causing instability in the functioning of the tetrode. This led to the development of the pentode with the addition of a third grid called *suppression grid*, which was meant to suppress the secondary emission current. Favoured over the tetrode, the pentode was invented in 1928 by T.D.H. Tellegen. There are also other multifunction and multisection vacuum tubes with as many as five grids called the pentagrid converter, as shown in Fig. 1.2. This is used in superheterodyne receivers that require a local oscillator and a mixer, equivalent to two tubes.

Vacuum tubes perform basic functions of rectification, amplification, switching, and mixing. The development of vacuum tubes in the 1920s led to their applications in the commercialization of radio transmission/broadcasting and receiving, televisions, computers, and many other electronic devices. One important advantage of vacuum tubes is that they are less susceptible to be affected by electromagnetic pulses or nuclear radiations. That is perhaps the reason why the military continued to use them long after they were replaced by transistors.

The use of microwave frequencies in radar and communications applications led to the development of special microwave tubes that overcame the limitations of the conventional tubes, such as dependence of interelectrode capacitance, lead inductance, and electron transit-time effects. Microwave tubes, such as the klystron and travelling wave tube (TWT) take advantage of transit-time effects, making use of velocity modulation to amplify and generate microwave energy. The klystron may be used as an amplifier or oscillator. TWT is a wide-bandwidth tube primarily used as an amplifier. The magnetron is a diode oscillator capable of delivering microwave energy at very high power levels.

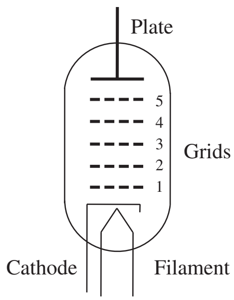


FIG. 1.2 Pentagrid converter showing 5 grids

Electron tubes were used in different designs of computers during the 1940–1950s, which continued to be in use until the 1960s. As the circuits became more complex, a large number of triodes was needed, with over 15,000 tubes in big computers, occupying about 160 square metre space, running on 150 KW power, operating at maximum 100 KHz frequency, and generating a huge amount of heat. For example, the vacuum tube-based electronic numerical integrator and computer (ENIAC) performed only 1000 mathematical operations per second, when compared to approximately one billion operations per second performed by recent computers. Leaking of the tubes and burnout of the cathode added to the serious reliability issues of these vacuum tubes. Thus, the use of vacuum tubes had reached its ultimate limit. In spite of their limitations, vacuum tubes are still used in some specific applications. For example, they are in use even in present-day microwave communication technologies of mobile phones, Wi-Fi, radar, and satellite transmission systems, as high-power microwave sources. There are also other vacuum tube devices, which include X-ray tubes, cathode ray tubes (CRT), photo multipliers, TV screens, and computer monitors as displays.

1.2.2 Quantum Theory

The story of quantum began in 1900 and 25 years later arrived at a new science called *quantum mechanics*, *wave mechanics,* or *quantum physics*, which brought about a scientific revolution in probing molecules, atoms, and subatomic particles. Quantum mechanics also formed the basis of the modern theory of solids and the invention of the transistor.

Old Quantum Mechanics

Max Planck laid the foundation of quantum mechanics in 1900 postulating the law of blackbody radiation, which states that energy is radiated or absorbed only in integral multiples of an elementary 'quantum' or 'photon' of energy, $\varepsilon = \mathrm{h}v$, in agreement with experimental observations [Planck 1901]. Here, h is a constant of proportionality called Planck's constant and v is the frequency of radiation. If there are N photons, the total energy is $E = N\mathrm{h}v$. His insights gave the first glimpse of the onset of an epoch-making era, now known as the information age. He was awarded the Nobel Prize for Physics for his discovery in 1918.

In order to explain the photoelectric effect, discovered earlier by Heinrich Hertz in 1887, Albert Einstein postulated in 1905, consistent with Planck's quantum hypothesis, that light is made of quantum particles called quanta (photons). He was awarded the Nobel Prize for Physics in 1921. It may be recalled that Nicholaus Copernicus (1473–1543), Galileo Galilei (1564–1642), Johannes Kepler (1571–1630), and Isaac Newton (1642–1727) dismantled the Aristotalian model of the universe and gave birth to the celestial classical mechanics. Kepler discovered that each planet orbits the sun following an elliptic path with the sun at one focus of the ellipse, and that the planets move more quickly when closer to the sun. This is known as Kepler's theory of solar planetary motion.

In the 1660s, Isaac Newton extended the Kepler model of planetary motion and explained using gravity, why planets have elliptical orbits. The classical mechanics is, therefore, sometimes called Newtonian mechanics after his three laws of motion and gravitation. According to Ernst Rutherford's atomic model of 1911, a tiny dense nucleus less than 3.4×10^{-14} m is surrounded by a lot of empty space, sprinkled by orbiting electrons at some distance. Building on Rutherford's atomic theory, Planck's law of quantization of radiation, and the classical mechanics of Kepler and Newton, Neils Bohr put forward his theory for the hydrogen atom in 1913, marking the beginning of a new era in spectroscopy and atomic structure. Bohr concluded that the hydrogen atom was made up of a nucleus having one positively charged proton at the centre and a negatively charged electron moving around the nucleus in closed circular quantized energy orbits. Bohr was awarded the Nobel Prize for Physics in 1922 for his atomic theory. Subsequently, to account for the fine structure of energy levels of hydrogen and hydrogen-like atoms, Arnold Sommerfeld extended Bohr's theory of the hydrogen atom, to include elliptic orbits of electrons and relativistic correction to electron velocity. The splitting of atomic levels in the presence of a homogeneous magnetic field known as the normal Zeeman effect could be explained in terms of three quantum numbers—total quantum number (n), orbital angular momentum number (l), and orbital magnetic quantum number (m_l). However, the splitting of atomic levels in the presence of an inhomogeneous magnetic field known as the anomalous Zeeman effect, as observed in Stern–Gerlach experiment, could not be explained using these three quantum numbers (n, l, m_l). Thus, it was clear by the early 1920s that there was a problem with space quantization of the three-dimensional motion of electrons around the nucleus.

Wolfgang Pauli was the first to suggest the need for the introduction of a fourth quantum number in addition to the quantum numbers n, l, and m_l. Samuel Goudsmit and George Uhlenbeck proposed that the electron must have an intrinsic spin quantum number, $s = ½$. Since a spinning electron possesses a magnetic moment m_s, an atomic level should split into $2s + 1 = 2$ levels corresponding to $m_s = \pm 1/2$ in an external magnetic field, analogous to the splitting into $2l + 1 = 3$ levels corresponding to $m_l = 0, \pm 1$ for $l = 1$. The electron's spin will be oriented either 'up' or 'down' in a magnetic field. Thus, there is a set of four quantum numbers (n, l, m_l, m_s), which must be unique for each electron in an atom. Besides contributing to settling the space quantization problem, Pauli put forward a broad principle, later called the *Pauli's exclusion principle*. According to the exclusion principle, the set of four quantum numbers describing a state occupied by an atomic electron must be unique for that electron, that is, no two electrons in an atom may have the same set of quantum numbers (n, l, m_l, m_s). Later, it was established that Pauli's principle applies to any system of electrons. In other words, the electrons in all systems (atoms, molecules, or solids) must organize themselves, obeying the Pauli's exclusion principle. Pauli was awarded the Nobel Prize for Physics for the exclusion principle in 1945.

Wave Mechanics

In 1924, Louis de Broglie put forward his theory of the dual nature of matter, stating that particles can exhibit wave characteristics and vice versa, that is, matter, like energy, exhibits a wave–particle duality. For his wave–particle duality principle, he was awarded the Nobel Prize for Physics in 1929. While Werner

Heisenberg, Max Born, and Pascual Jordan at Göttingen developed matrix mechanics, at the same time in 1926 in Zurich, Erwin Schrödinger invented wave mechanics and derived a non-relativistic wave equation known after him as the Schrödinger equation, known as a generalization of de Broglie's theory. He further established that the two approaches were equivalent. Subsequently, proposing the Dirac equation for electrons, Paul Dirac unified wave mechanics with the special theory of relativity. Schrödinger and Dirac shared the Nobel Prize for Physics for their work in 1933. In wave mechanics, a moving electron in an atom is represented by a matter wave that is represented by a wave function and may be viewed as the cloud of charge around the nucleus. The wave function determines the likelihood or probability of finding a particle at a given position in space at a given time. Thus, when applied to a quantum system, the solutions of the Schrödinger equation are distributions of probabilities for electron positions and locations with time. Max Born, one of the founders of quantum theory, was the first to introduce the probability interpretation in 1926. He was awarded the Nobel Prize for Physics in 1954.

Heisenberg's Uncertainty Principle

There is a basic difference between classical mechanics and quantum mechanics. Classical mechanics presumes that exact simultaneous values can be assigned to all physical properties of a classical system, whereas quantum mechanics forbids such possibilities. Heisenberg postulated the uncertainty principle in 1927. It limits the precision with which certain pairs of physical properties of a particle, known as complementary variables such as position (x) and momentum (p) or energy (E) and time (t), can be determined simultaneously. In other words, the position and momentum of a particle can't be simultaneously measured with an arbitrary fixed precision. It means that the product of the uncertainty in measurement of these two quantities has to be a certain minimum, that is, $\Delta x \Delta p \geq \hbar/2$.

Similar arguments hold good for accuracy in simultaneous measurements of energy and time, that is, $\Delta E \Delta t \geq \hbar/2$. However, this fixed limit of uncertainty should not be mistaken for the inaccuracy incurred in the measurements caused by the instruments used or the limitation introduced by the experimental techniques. It originates rather from the wave properties inherent in the quantum nature of the particle. Stated differently, the uncertainty limit is fundamental and, therefore, inherent in the nature of matter and even perfect techniques and instruments will not help in reducing it below the limits fixed by the uncertainty principle. Heisenberg was awarded the Nobel Prize for Physics in 1932.

A host of other scientists contributed significantly towards the development of quantum mechanics. Notable among those are Arthur Compton, John von Neumann, Enrico Fermi, Max von Laue, Freeman Dyson, David Hilbert, Wilhelm Wien, Satyendra Nath Bose, and others.

These theoretical advances in quantum mechanics were followed by the development of quantum theory of solids, which played a critical role in the invention of several semiconductor devices, including the transistor—the biggest invention of the 20th century.

1.2.3 Invention of Transistor

The emergence of solid-state electronics may be traced back to the invention of the point-contact rectifier on galena, a naturally occurring crystalline mineral of lead sulphide (PbS), in 1874 by Karl Ferdinand Braun from Germany. This device was the forerunner to the cat's whisker detectors, used in crystal receiver sets in mid 1920s. Such early point-contact diode detectors were fabricated by pressing a spring-loaded conducting hard wire (resembling a cat's whisker) on a semiconductor to form a pn junction, hence being named the *cat's whisker detector*. However, the device was not very stable in that configuration. In addition, unfortunately, after the invention of the vacuum tube, the device was rendered obsolete. However, as people were in search of devices working at higher frequencies and the vacuum tubes did not meet this requirement, the point-contact rectifiers eventually resurfaced again and came to the fore.

J.C. Bose, the renowned physicist from India, invented solid-state detectors, called *coherers*, in 1894–96 for a wide spectrum of electromagnetic radiations for the reception of Hertzian waves (now called millimetre waves), light waves, and other radiations and obtained the US patent for his invention in 1904 [Bose 1904]. 'J.C. Bose was at least 60 years ahead of his time. In fact, he had anticipated the existence of P-type and N-type semiconductors,' remarked N.F. Mott about his contribution to solid-state electronics [Emerson 1997]. Bose was the first person to generate, detect, and characterize millimetre waves (60 GHz) accurately. While on a lecture tour in the UK in 1991, he stated, 'How lucky we are that the natural eye absorbs this radiation and protects us by veiling our sense against insufferable radiance in these days of space signaling by Hertzian waves' [Bose 1927]. The work of Bose that led to the development of the galena (PbS) detector and the impact of his contribution to millimetre wave and microwave detection has been discussed by Sengupta and coworkers [Sengupta et al. 1998]. First experiments on free space transmission of radio waves for signalling purposes were conducted by Nikola Tesla in 1893 [IEEE 2003], and Bose repeated these experiments in 1884 using microwaves [Emerson 1997]. Subsequently in 1887, G. Marconi performed his famous demonstration of wireless transmission for communication applications at Salisbury Plain in the UK. Both, G. Marconi, and Ferdinand Braun, shared the Nobel Prize for Physics in 1909 for their contribution to the development of wireless telegraphy.

J.C. Bose (1858–1937)

J.C. Bose graduated in Physical Science in 1879 from St. Xavier's College, Calcutta, received BA in Natural Science from the Christ's College of Cambridge University, and B Sc from London University in 1884. On his return to India in 1985, Bose joined the Presidency College as a Professor of Physics. S.N. Bose, best known for the Bose–Einstein statistics, and Meghnad Saha, best known for his development of the Saha equation for thermionic emission, were his students. Bose was knighted in 1917 and became the first Indian to be elected for membership of the Royal Society in 1920.

J.C. Bose conducted many fundamental research investigations at the Presidency College and established the tradition of scientific research in India towards the end of the 19th century. Inspired by the experimental demonstration of electromagnetic waves in free space by Heinrich Hertz in 1888 and public demonstration of radio communication by Nikola Tesla in 1893, Bose followed his interest in electromagnetic wave research, making use of millimetre waves (mm-waves). He rightly believed that it would be advantageous to use mm-waves as the physical size of various components required for the experimental work would be smaller than needed with longer microwaves (in centimetres). He not only succeeded in generating mm-waves, but also developed mm-wave circuit components. He perfected a complete mm-wave transmission and reception system working at 60 GHz. He also developed and patented the galena crystal diode detector for making a communication receiver set suitable for the detection of short radio waves, visible, and UV radiation of electromagnetic spectrum, a forerunner of the semiconductor mm-wave diode detector. Bose gave his first demonstration of the use of electromagnetic waves at the Town Hall in Calcutta in 1895 by remotely ringing a bell and exploding gun powder. Further work on millimetre wavelengths was nearly absent for the next 50 years.

By the turn of the 19th century, Bose's interest shifted away from electromagnetic waves to response phenomena in plants. He demonstrated that plant tissues under different kinds of stimuli, such as heat, electric shock, chemicals, and drugs, produce electrical responses similar to those produced by animal tissues. For these investigations, he invented several novel and highly sensitive instruments.

The theoretical development of quantum mechanics during the 1920s also played an important role in providing a boost for solid-state electronics. The comprehensive understanding of solids without the development of quantum mechanics would not have been possible. The basic concepts of electronic band structure were developed using quantum mechanics. Band theory of solids helps us understand what makes a conductor, semiconductor, or insulator and the reasons behind their differences. The advances in quantum mechanics were followed by the development of quantum theory of solids led by Rudolf Peierls, A.H. Wilson, N.F. Mott, J. Franck, and others. Applying band theory of solids, Wilson formulated transport theory of semiconductors. Later in 1938, Walter Schottky developed the theory of metal–semiconductor contacts and gave an explanation of their rectifying behaviour that depends on the energy barrier between the two materials. The barrier height is a function of the metal–semiconductor work function difference and the image-force induced barrier lowering, called the *Schottky effect*. However, his theory yielded only qualitative understanding of the rectifiers discussed previously. Even though the dedicated efforts of these researchers brought the understanding forward, a lot more was still desired to understand the behaviour of semiconductors clearly in those days.

The original idea of a field effect transistor (FET) came to the German scientist Julius E. Lilienfeld in 1925 [Lilienfeld 1926]. He expected that the conductivity of a poorly conducting material could be modified by applying a voltage, which may be used to achieve amplification. However, for a long time, nobody was able to utilize his idea in making a working device. Next, a structure resembling a metal-oxide semiconductor field effect transistor (MOSFET) was proposed by Oskar Heil in 1935, but material problems foiled his attempt in making a functional device. Then in 1938, Robert Pohl and Rudolf Hilsch worked on potassium bromide crystals with three electrodes at Gottingen University, Germany [Hilsch et al. 1938]. They reported amplification at low-frequency (about 1 Hz) signals, but their research did not lead to any applications. It was already realized by the late 1930s that the vacuum tube could not offer the ultimate solution to electronics due to problems related to reliability, higher power dissipation, lower frequency response, and size. At this time, Mervin Kelly at Bell Labs in 1936 decided to form a group of scientists and engineers to work on solid-state devices, which included William Shockley, Russell Ohl, Jack Scaff, and others. Great efforts were made in an attempt to understand the growth of the silicon crystal.

William Shockley (1910–1989)

Born in London in 1910, William Shockley was educated at the California Institute of Technology in Pasadena earning his B Sc degree in Physics in 1932. Then, he entered MIT for his doctoral work under the supervision of a famous physicist John C. Slater and obtained the Ph D degree in 1936, submitting a thesis on 'the energy band structure of sodium chloride'. The same year, he joined Bell Labs to work initially on the design and development of an electron multiplier tube. However, he soon became involved in research in semiconductor physics as the Administrative Head of the team. His idea of field effect transistor, similar to the field effect device patented by J.E. Lilienfeld in 1930, failed to work due to high density of surface states, which shielded the applied electric field, as suggested by his colleague John Bardeen. Taking a clue from the influence of surface states, John Bardeen and Walter Brattain worked hard and were successful in demonstrating the working of a point-contact transistor. Soon after, Shockley developed the layered bipolar junction transistor and worked out the theory of the transistor. The transistor behaved exactly as predicted by his theory. Shockley was awarded the Nobel Prize for Physics for this work in 1956, which he shared with his colleagues at Bell labs, John Bardeen, and Walter Brattain. In 1963, Shockley was appointed as Professor of Engineering at Stanford University where he taught until 1975.He was a superb teacher who inculcated creativity in his students.

Besides the Nobel Prize, he was honoured with the Medal for Merit for his work with the War Department (1946), Oliver E. Buckley Solid State Physics Prize of American Physical Society (1953), Maurice Liebman Memorial Prize of IEEE (1980), and many other awards.

It was observed that the crystal could be p-type or n-type depending on the way it was prepared. The meaning of a crystal being p-type or n-type in those times was whether it formed a positive (p) or negative (n) rectifier. Later, the crystal growth could be controlled to prepare a sample in which p-type would be on the top of n-type, which would develop voltage on illumination with light [Scaff et al. 1949]. It was discovered, while slicing wafers from n-type ingot, that it smelt like phosphate, from which the impurity was inferred to be phosphorus with an extra electron as compared to silicon. This is how the materials were identified at that time. The researchers at Purdue University contributed significantly to understand the role played by the presence of surface states in the working of silicon and germanium devices. This was the scenario of solid-state devices prior to World War II. During the war, the emphasis shifted to improve upon radar performance using finely-tuned point-contact rectifiers and low capacitance solid-state detectors in gigahertz regime.

After the war in 1946, Mervin Kelly regrouped the team to work on his unfinished agenda of solid-state electronics with William Shockley and Stanley Morgan as the group leaders and John Bardeen, Walter Brattain, and others as the team members. In preference to compound semiconductors, such as lead sulphide or copper oxide, they decided in the first place to concentrate their work on the simple elemental semiconductors—silicon (Si) and germanium (Ge)—with bandgaps of 1.12 eV and 0.66 eV, respectively. Shockley independently revived the idea of a field-effect device, but failed to achieve his predicted result experimentally. The idea was to apply a voltage to a semiconductor that would result in a change in its conductivity (as suggested earlier and patented by Lilienfeld in 1926) and this should have been demonstrable in the laboratory, but it was not the case. With the results on semiconductor surface states obtained by the group of researchers at Purdue University and his own work in collaboration with W.H. Brattain before him, Bardeen made a simple calculation and showed that a relatively low density of surface states would screen any field from penetrating the interior of a semiconductor. This understanding of the field effects was a significant contribution made by Bardeen and Brattain. To overcome the effect of surface states, they soon started investigating on ways to obtain clean surfaces of Ge crystal blocks to make a working device, and by the end of 1947, Bardeen and Brattain succeeded in making the first working point-contact transistor. This transistor used germanium crystal block as the base lead and the other two contacts (about 50 μm apart) on the top of germanium block were formed by pressing the tip of a plastic wedge with gold foil sheared with a razor at its tip and these served as emitter and collector leads. The device was used in a prototype audio amplifier circuit demonstrating actual voice amplification. On June 30 1948, Bell Labs made a public announcement of the invention of the transistor. This was perhaps the biggest event of the 20th century! The image of the first point-contact transistor is shown in Fig. 1.3.

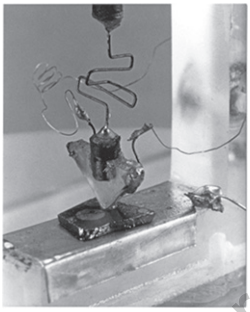


FIG. 1.3 The first Ge point-contact transistor
Courtesy: Reprinted with permission of Alcatel-Lucent USA Inc.

John Bardeen (1908–1991)

Born in 1908 in Madison, Wisconsin, John Bardeen earned a BS degree in 1928 and MS in 1929, both in Electrical Engineering from the University of Wisconsin at Madison. He chose engineering that involved a lot of mathematics, which he loved. As his interest shifted to pure science, he decided on his doctoral work in mathematical physics at Princeton University under physicist E.P. Wigner and developed an interest in solid-state physics. Before completing the thesis, he was offered a junior fellowship at Harvard University to work with Professor J.H. van Vleck and Percy Williams Bridgeman on electrical conduction in metals and stayed there for three years until 1938. Meanwhile, he was awarded the PhD degree of Princeton University in 1936. Bardeen joined the Solid-state Physics Group of Bell Labs led by William Shockley and Stanley Morgen in 1945. The group was developing a solid-state replacement for vacuum tube amplifier. After the initial unsuccessful attempts at developing the field effect transistor proposed by Shockley, Bardeen, and his fellow researcher Walter Brattain, studied the surface states that screened the applied field from penetrating the semiconductor and caused device failure. They succeeded in their effort in controlling surface states using an electrolyte at the metal electrode point-contact to the semiconductor and produced a working point-contact transistor (transfer-resistor) in 1947. Subsequently, within months, Shockley independently developed a layered bipolar junction transistor bypassing surface states completely and formulated the transistor theory, which explained the transistor behaviour very successfully. The three inventors of the transistor—Shockley, Bardeen, and Brattain—were jointly awarded the Nobel Prize for Physics in 1956.

In 1951, Bardeen was appointed as Professor of Electrical Engineering, and simultaneously, as Professor of Physics at the University of Illinois at Urbana-Champaign and was working on superconductivity in metals. His work with L.N. Cooper and J.R. Schrieffer resulted in the BCS theory of superconductivity. Bardeen was awarded the second Nobel Prize for Physics for BCS theory in 1972, which he shared with Cooper and Schrieffer. He was also honoured with the Franklin Institute's Stuart Ballantine Medal (1952), National Medal for Science (1965), IEEE Medal of Honour (1971), Presidential Medal of Freedom (1977), and numerous other awards, and was elected as a fellow of American Academy of Arts and Science.

After his return from a short trip to Europe in 1947, Shockley started working on the theory of bipolar transistor, and in the next two months, he began writing the theory based on the concept of minority carrier injection into the semiconductor. He verified his theory of minority carrier injection from measurements on a transistor with emitter and collector on the opposite sides of the Ge crystal, thus eliminating the surface path between emitter and collector as in the first transistor. The device behaved essentially as predicted by Shockley's theory. The famous relation describing the I–V characteristics of a bipolar diode is known after him as Shockley's diode equation. Shockley, Bardeen, and Brattain were awarded the Nobel Prize for Physics in 1956 for their invention of the transistor. An intriguing narration of the story of the invention of the transistor was reported by Brinckman and his coworkers [Brinkman et al. 1997].

Walter Brattain (1902–1987)

Walter H. Brattain was born in Amoy, China, in 1902. Soon after his birth, his parents returned to Washington State. He received his B S from Whitman College in 1924, M S in Physics from Portland University in 1926, and Ph D from the University of Minnesota in 1929. In 1928, he joined the National Bureau of Standards as a Radio Engineer. One year later in 1929, he joined Bell Labs. He was basically an experimental physicist and was working in the Solid-state Physics group with an assignment to develop a solid-state amplifier as the replacement for a vacuum tube, under the guidance of William Shockley and Stanley Morgen. Their understanding of surface properties of semiconductors was helpful in developing a working point-contact transistor in 1947. For this work, they shared the Nobel Prize for Physics with William Shockley and John Bardeen in 1956.

Dr Brattain was a member of the National Academy of Sciences, the Franklin Institute, the Commission on Semiconductors of International Union of Pure and Applied Sciences, and the Naval Research Advisory Committee. In addition, he was a fellow of the American Physical Society.

Further progress continued in improving bipolar transistors at Bell Labs and the team succeeded in growing an npn junction device in 1950, which functioned truly as expected. Germanium crystal purity was improved significantly by a reduction of background impurities level from a few parts per million (ppm) to a few parts per billion (ppb) by a process called 'zone refining' developed by William G. Pfann, a material scientist with Bell Labs [Pfann 1978]. Subsequently, Ross and Dacey made the first unipolar junction field effect transistor (FET), a precursor to the present MOSFET [Dacey et al. 1953]. These junction FETs work in the pinch-off mode, as compared to MOS transistors, which use enhancement or depletion mode of operation.

Soon after its invention, the bipolar transistor was in use in some products, such as hearing aids, transistor radios, and telephone exchanges. Texas Instruments demonstrated an all-transistor radio as early as in 1952. The Regency TR-1, which used Texas Instruments' npn transistors, was the first commercially produced transistor radio by Industrial Development and Engineering Associates (I.D.E.A.) of Indianapolis, in 1954. Sony's all-transistor radio was introduced in the late 1950s, with a good marketing strategy to popularize it, creating a consumer market for transistors. Subsequently, there was widespread use of discrete transistors in a large number of commercial products all over the world.

The next historic landmark development took place in the late 1950s, when native silicon dioxide was grown on silicon at a high temperature under oxidizing ambient first by C.J. Frosch, and subsequently, M.M. Attala and D. Kahng fabricated a Si–SiO_2 field-induced device, later termed as MOSFET [Kahng et al. 1960]. The device performance, however, was quite poor, due to the difficulty caused by the presence of mobile ion impurities, such as sodium, that caused a shift in device characteristics drastically, particularly when present at the Si–SiO_2 interface. It took a very long time to identify the cause and solve the problem until the early 1970s by making the materials as well as the processing systems used in fabricating devices, free from sodium contamination. A lot of efforts were put in by different groups working on silicon technology to obtain defect-free, perfect Si–SiO_2 interface, a necessary condition for making good devices, as evidenced by a very large number of research papers published during the 1970s on the subject from across the world.

1.2.4 Integrated Circuit Era

Jack Kilby developed and demonstrated the first integrated circuit (IC) at Texas Instruments in September 1958 with three components comprising a mesa-structured transistor, a capacitor, and a resistor, all on the same Ge monolithic block. The discrete wires were used to connect the components. Although the IC was modest as compared to today's standards, Kilby's idea was ground-breaking. Following that, Jean Hoerni developed the planar process for making transistors at Fairchild. Making use of this process, Robert Noyce came up with his idea of the integrated circuit in 1959 to interconnect all the components on the chip using evaporated metal, replacing the discrete wire used by Kilby. Frank Wanlass and C.T. Sah were the first to fabricate logic gates using MOSFETs in 1963 at Fairchild [Wanlass et al. 1963]. They used both the nMOS and pMOS gate transistors called the complementary symmetry MOS (CMOS). The circuit used discrete transistors but consumed only nanowatt (nW) power in standby mode, which is about six orders less than their bipolar counterpart. With the development of planar technology, MOS integrated circuits (MOS-ICs) became very attractive, due to a simpler process of fabrication, with the transistor occupying a lesser area, and consuming much lower power, as compared to bipolar technology. In less than three decades since 1960, the number of transistors had risen from a meagre number of ten to millions of transistors on a chip, keeping pace with Gordon Moore's law. Moore observed in 1965 that the number of transistors on a chip would double every 18 months [Moore 1960]. Depending on the number of transistors or logic gates, the level of integration on chips is classified as small scale integration (SSI), medium scale integration (MSI), large scale integration (LSI), very large scale integration (VLSI), and ultra large scale integration (ULSI). As the device size is scaled down to put more components on the chip, the transistors become faster, more economic, and consume less power with the passage of time. Of course, this scaling cannot go on forever, as fundamental physical and electronic limits of materials approach. For example, for the gate oxide thinner than 2 nm, the tunneling currents between the gate and substrate would start dominating, leading to the failure of MOSFET. Further discussion on number of components on the chip and present status of VLSI technology is presented in Section 14.5 in Chapter 14. Intel's high-end Itanium 9300 processor, which is code-named *Tukwila* contains more than two billion transistors.

Some of the major discoveries and inventions, which led to a significant improvement in the understanding of materials and/or development of device technologies, are reflected in Table 1.1. The important discoveries and inventions of the scientists, apart from their Nobel Prize work, are also included. The table shows some of the major discoveries and inventions, either related to the fundamentals of quantum mechanical phenomenon, which are the conceptual foundation for nanostructures and devices, or those directly linked to the growth of nanotechnology since its inception, including some concerning nanomaterials used prior to the arrival of nanotechnology.

Table 1.1 Significant discoveries and the scientists

Discovery/Invention/Contributions	Nobel Prize winner(s)	Year
Colloids of gold and silver	Michael Faraday	1856
Investigations and discoveries in relation to tuberculosis	Robert Koch	1905
Investigation on the conduction of electricity by gases / discovery of electron	Joseph J. Thomson	1906
Investigation into the disintegration of the elements, chemistry of radioactive substances and the structure of atom	Ernest Rutherford	1908
Advancement of physics by the discovery of energy quanta	Max Planck	1918
Fundamental contributions to theoretical physics, especially the discovery of the law of the photoelectric effect, and the theory of relativity	Albert Einstein	1921
Investigation of the structure of atoms and of the radiation emanating from them	Niels Bohr	1922
Discovery of the wave-nature of electrons	Louis de Broglie	1929
Scattering of light and for the discovery of the Raman effect	Chandrashekhara V. Raman	1930

(*Contd*)

Table 1.1 (*Contd*)

Discovery/Invention/Contributions	Nobel Prize winner(s)	Year
The creation of quantum mechanics, the application of which has led to the discovery of the allotropic forms of hydrogen	Werner K. Heisenberg	1932
Theory of wave mechanics	Erwin Schrödinger and P.A.M. Dirac	1933
Demonstration of the existence of new radioactive elements produced by neutron irradiation, discovery of nuclear reactions brought about by slow neutrons, and important contributions to the development of quantum mechanics	Enrico Fermi	1938
The discovery of the Exclusion Principle, also called the 'Pauli Principle'	Wolfgang Pauli	1945
Development of new methods for nuclear magnetic precision measurements and the Bloch theorem	Felix Bloch	1952
Fundamental research in quantum mechanics, especially for the statistical interpretation of the wave function	Max Born	1954
Research on semiconductors and the discovery of the transistor effect	William B. Shockley, John Bardeen, and Walter H. Brattain	1956
The fundamental work in the field of quantum electronics, which has led to the construction of oscillators and amplifiers based on the maser–laser principle	Charles H. Townes, Nicolay G. Basov, and Aleksandr M. Prokhorov	1964
Fundamental work in quantum electrodynamics, with deep-ploughing consequences for the physics of elementary particles	Sin-Itiro Tomonaga, Julian Schwinger, and Richard P. Feynman	1965
Contributions to the knowledge of electronic structure and geometry of molecules, particularly free radicals	Gerard Herzberg	1970
Development of the theory of superconductivity, usually called the BCS theory	John Bardeen, Leon N. Cooper, and John R. Schrieffer	1972
Theoretical predictions of the properties of a super current through a tunnel barrier, particularly those phenomena which are generally known as the Josephson effects	Brian D. Josephson	1973
Experimental discoveries regarding tunneling phenomena in semiconductors (L. Esaki) and superconductors (Ivar Giaever)	Leo Esaki and Ivar Giaever	1973
Fundamental theoretical investigation of the electronic structure of magnetic and disordered systems	Philip W. Anderson, Nevill F. Mott, and John H. van Vleck	1977
Discovery of the quantized Hall effect	Klaus von Klitzing	1985

(*Contd*)

Table 1.1 (*Contd*)

Discovery/Invention/Contributions	Nobel Prize winner(s)	Year
Discovery of fullerenes	Robert F Curl Jr, Harold W. Kroto, and Richard E. Smalley	1996
Discovery of superfluidity in helium-3	David M. Lee, Douglas D. Osheroff, and Robert C. Richardson	1996
Discovery of a new form of quantum fluid with fractionally charged excitations	R.B. Laughlin, H.L. Störmer, and D.C. Tsui	1998
Developing semiconductor heterostructures used in high-speed- and opto-electronics	Zhores I. Alferov and H. Kroemer	2000
Basic work on information and communication technology inventing of the integrated circuit	Jack S. Kilby	2000
The achievement of Bose–Einstein condensation in dilute gases of alkali atoms, and for early fundamental studies of the properties of the condensates	Eric C. Cornell, Wolfgang Ketterle, and Carl E. Wieman	2001
Pioneering contributions to the theory of superconductors and superfluids	Alexei A. Abrikosov, Vitaly L. Ginzburg, and Anthony J. Leggett	2003
Contribution to the quantum theory of optical coherence	Roy J. Glauber	2005
Discovery of giant magnetoresistance	Albert Fert and Peter Grünberg	2007
Ground-breaking experiments regarding the two-dimensional material grapheme	Andre Geim and Konstantin Novoselov	2010
Ground-breaking experimental methods that enable measuring and manipulation of individual quantum systems	Serge Haroche and David J. Wineland	2012

1.3 PHYSICAL SIZE SCALES

Depending upon how many physical dimensions of nanostructures lie within the nanoscale, and consequently, degree(s) of charge carrier confinement, they are further classified into three categories—one-dimensional quantum wells, two-dimensional quantum wires, and three-dimensional quantum dots nanostructures—that will be discussed in detail in Chapter 3. Conversely, the degree(s) of free movement of charge carriers in a nanoparticle will be the same as the number of physical dimensions of size larger than 100 nm. For example, a quantum well has one degree of carrier confinement, and two degrees of free carrier movement, and so on.

In order to visualize the size-scale of nanomaterials with respect to the vast size variation of objects existing in the universe, we should look at the different size-scales in use, prior to the formal arrival of nanomaterials in the late 1980s. In a broader sense, material objects can be represented on two size-scales, leaving aside the astronomical and subatomic scales on the two extremes, namely, *macroscopic* and *microscopic*. The macroscopic scale refers to the large objects visible to the naked eye. The lower size limit of these objects, which are visible to the naked eye is around 10 μm (Symbol μ stands for factor micro = 10^{-6}, m for metre, and μm normally called *micron*, being a millionth of a metre). Thus, all objects larger than ten micron fall within the macroscopic scale, such as the height of a human being, the size of a tennis ball, a house fly, and a human hair. The human hair's thickness lies in the range of 15–180 μm, with the lower side being close to the visibility limit of the unaided eye. All the macroscopic objects obey the laws of classical mechanics characterized with average or bulk properties. Different factors used in scientific notations are given in Table 1.2

Table 1.2 Factors used in scientific notation to express small and large numbers in metric system

Prefix (symbol)	Factor	Name	Prefix (symbol)	Factor	Name
deca (da)	10^1	ten	deci (d)	10^{-1}	Tenth
hecto (h)	10^2	hundred	centi (c)	10^{-2}	hundredth
kilo (k)	10^3	thousand	milli (m)	10^{-3}	thousandth
mega (M)	10^6	million	micro (μ)	10^{-6}	millionth
giga (G)	10^9	billion	nano (n)	10^{-9}	billionth
tera (T)	10^{12}	trillion	pico (p)	10^{-12}	trillionth
peta (P)	10^{15}	quadrillion	femto (f)	10^{-15}	quadrillionth
exa (E)	10^{18}	quintillion	atto (a)	10^{-18}	quintillionth
zetta (Z)	10^{21}	sextillion	zepto (z)	10^{-21}	sextillionth
yotto (Y)	10^{24}	septillion	yocto (y)	10^{-24}	septillionth

The objects that are smaller in size than the eye's visibility limit and that require a microscope to be detected or observed clearly, down to individual atoms, fall within the microscopic scale. Presently, electron microscopes are capable of imaging even the individual atoms. The scanning-probe-type electron microscopes, particularly, the atomic force microscope (AFM) and scanning tunnel microscope (STM), are used in scientific investigations to image objects as small in size as that of an atom. Thus, all objects with size variation between 10 μm and an individual hydrogen atom of 0.1 nm may be considered to lie on the microscopic scale. As the size of objects decreases, they continue to obey the laws of classical mechanics with average/bulk properties, independent of particle size. The number of atoms on the surface of such particles is quite negligible, as compared to the number of atoms lying inside the particle, the bulk properties being dominant. As the particle size approaches a sub-micron limit of about 0.1 μm (100 nm), a transition occurs in material properties, shifting their size-independent classical behaviour to size-dependent quantum-mechanical behaviour. The surface-to-volume ratio of these particles increases with decrease in size, and their surface properties start dominating the bulk properties. This amounts to increase in the number of atoms on the surface as compared to those inside the particle. Obeying quantum mechanical laws would mean that they possess discrete energy states like those of atoms or smaller molecules. These material particles are called 'nanoparticles' and the scale representing them is known as 'nanoscale'. Thus, the lower part of the microscopic/mesoscopic scale below 100 nm is now distinctly designated as the 'nanoscale'. The three sizes of scales, that is, macroscopic scale (down to 10 μm), microscopic scale (10 μm down to 0.1 nm), and nanoscale (100 nm–0.1 nm) are shown in Fig. 1.4.

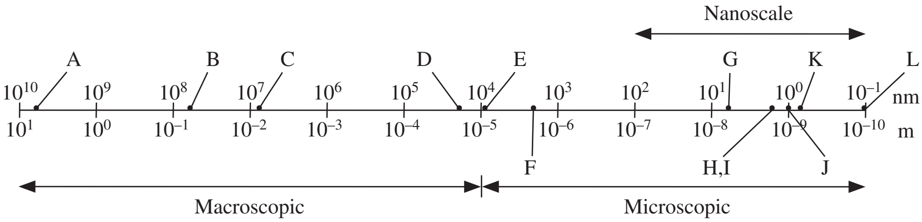


FIG. 1.4 Material objects on macroscopic, microscopic, and nanometre scales, indicated on the line in nanometres (above) and in metres (below). The nanometer scale (0.1–100 nm) is shown forming a part of microscopic scale.

In order to form an idea about the large difference in the sizes of worldly objects involved, they are represented by the dots on the scale for comparison and marked by alphabets A, B, C, D, etc. The relative sizes of these objects with respect to the hydrogen atom (diameter 1×10^{-10} m or 0.1 nm) are given in the last column of Table 1.3. A–D and E–L belong to macroscale and microscale, respectively. Objects G–L are common to both microscale and nanoscale. Our sun is nearly a perfect sphere with a diameter of about 1.392 million km, which is *1.392 × ten quintillion* times larger than the hydrogen atom. The figure *quintillion* represents 10^{18}.

Table 1.3 Comparison of the sizes of different objects to that of the hydrogen atom

Serial alphabet	Object	Size		Size relative to hydrogen atom (times)
		metre (m)	m/cm/mm/μm/nm	
A	Height of Indian male	1.66	1.66 m	1.66 × ten billion
B	Cricket ball	7.2×10^{-2}	7.2 cm	7.2 × hundred million
C	House fly	8.0×10^{-3}	8.0 mm	8.0 × ten million
D	Human hair	2.0×10^{-5}	20.0 μm	2.0 × hundred thousand
E	Red blood cell (RBC)	9.0×10^{-6}	9.0 μm	9.0 × ten thousand
F	Tuberculoses bacillus length	2.0×10^{-6}	2.0 μm	2.0 × ten thousand
G	Quantum dot	5.0×10^{-9}	5.0 nm	fifty
H	DNA helix diameter	2.0×10^{-9}	2.0 nm	twenty
I	Nanotube diameter	2.0×10^{-9}	2.0 nm	twenty
J	Bucky ball	1.0×10^{-9}	1.0 nm	ten
K	Amino acid molecule	8.0×10^{-10}	0.8 nm	eight
L	**Hydrogen atom**	$\mathbf{1.0 \times 10^{-10}}$	**0.1 nm**	**one**

cm = 10^{-2} m, mm = 10^{-3}m, μm = 10^{-6} m, and nm = 10^{-9} m

Some of these objects lying on the three different scales are shown in Fig. 1.5. Since only the objects larger than 10 μm are visible to the naked eye, it forms the lower limit of the macroscopic scale. The conventional microscopic scale (10–0.0001μm) has been split into microscopic scale (10–0.1μm) and nanoscale (100–0.1nm) scales, with transition at 0.1 μm (100 nm).

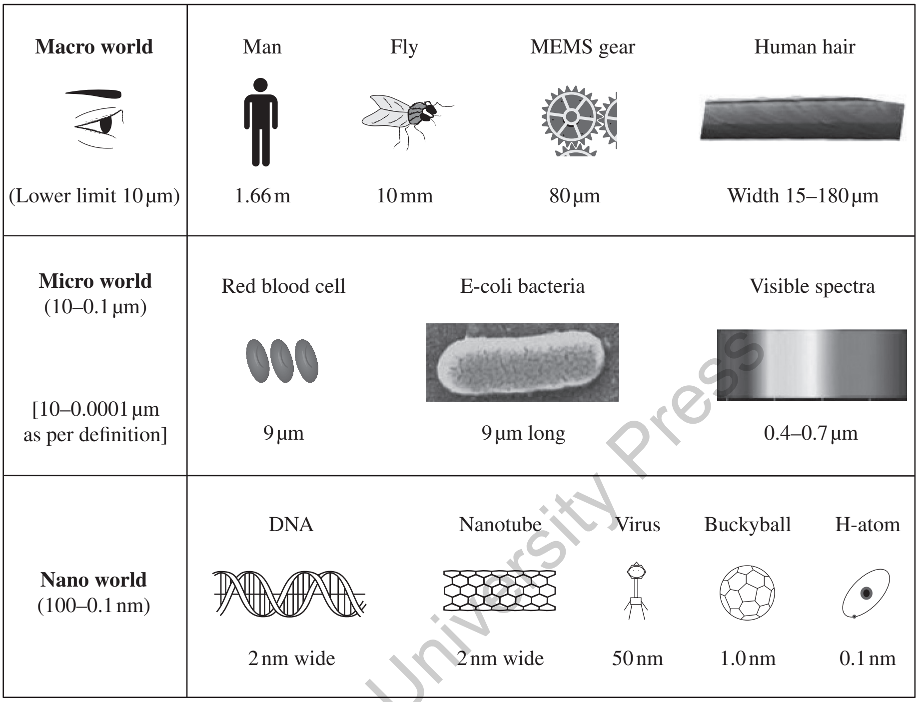


FIG. 1.5 Different material objects on macroscopic, microscopic, and nanometre scales

1.4 BIG VISION FOR THE SMALL WORLD

The recent origin of nanoscience and technology can be traced back to the predictions made by Richard P. Feynman, one of the greatest scientific geniuses of the 20th century. He demonstrated that there is scope to decrease the size of things in a practical way (what is possible according to the laws of physics). He envisioned that small structures could be formed in the future by arranging the atoms one by one, in the way we want. He was very confident and speculated that if we can have some control on the arrangement of things at a small scale, we will get an enormously greater range of i) possible properties that substances can have, and ii) different things that we can do. He thought about building electrical circuits on a small scale (nanoscale) that work at higher frequencies due to reduced transit time of the carriers in smaller components, resulting in very low time constant of the circuit. In addition, he envisioned that as we get to a very, very, small world, for example, a circuit consisting of a few atoms, this group of atoms on a small scale (read: the nanoparticles), forms an entirely new system that obeys the laws of quantum mechanics. By working with different laws, we can do different things involving quantized energy levels, interaction of quantized spins (values in multiples of ½), etc.

Feynman visualized writing or storing information at a small scale, instead of on the surface as usual, in three dimensions, using the interior of the material (layer by layer). Thus, enormous amount of the information could be carried in an exceedingly small space. Biological systems have this capability as a single cell has all the information of the organization of a complex creature, such as the human being.

Though not fabricated at the small scale (except one dimension of the quantum well, being on the nanoscale), the VLSI circuits may be packaged in three dimensions with chips stacked in vertical direction to compact a large system. However, dissipation of the huge amount of heat that gets generated in such stacked structures, with high packing density of components, is a big problem, and needs to be addressed.

In the 1950s, the resolution of electron microscopes was about 10 Å. During his talk, Feynman exhorted the scientific community to make the electron microscope 100 times better in order to enable us to make more rapid progress (to the point of imaging atoms). His logic was that since the wavelength of an electron in such microscopes is only 1/20 of an Å unit, it should be possible to see the individual atom. His dream was fulfilled when the first working scanning tunneling microscope (STM) belonging to the family of scanning probe microscopes was developed by Gerd Binnig and Heinrich Rohrer in 1981. They won the Nobel Prize for Physics in 1986 for their design of the STM. The resolution of 0.1 nm lateral, and 0.01 nm depth, is considered to be good for an STM equipment. With such resolution, individual atoms within materials are routinely imaged and manipulated. Electron-beam lithography technique, widely used in generating small feature-size masks presently, and also in the direct writing of circuits on the wafer, is yet another example of the application of electron waves in the fabrication of VLSI circuits, as envisaged by Feynman.

Richard P. Feynman (1918–1988)

Born in New York in 1918, Richard P. Feynman studied at MIT, receiving B Sc in Physics in 1939, and Ph D in Physics in 1942, from Princeton University, with his thesis being supervised by John Wheeler. Following that, he worked on the Manhattan Project. After the war, he was appointed as Professor of Theoretical Physics at the Cornell University (1945–1950). He joined the California Institute of technology (CALTECH) as Professor of Theoretical Physics (1950–1959), and subsequently, continued in the same university as 'Richard Chace Tolman', Chair Professor of Theoretical Physics. At CALTECH, he did significant work in quantum electrodynamics and physics of superfluidity of supercooled liquid helium.

Feynman introduced the concept of nanotechnology through his prophetic talk 'There is plenty of room at the bottom,' delivered on 26 Dec. 1959, at the annual meeting of the American Physical Society held at CALTECH. He popularized physics through his published lecture series for undergraduates titled *The Feynman Lectures on Physics*. He is also famous for his books *Surely You're Joking, Mr. Feynman* and *What Do You Care What Other People Think?*

He shared the Nobel Prize for Physics in 1965 with Sin-Itiro Tomonaga and Julian Schwinger for their fundamental work in quantum electrodynamics with significant contribution to the physics of elementary particles.

Feynman was a member of the American Physical Society, the American Association for the Advancement of Science, and the Royal Society, London. He was also awarded the Albert Einstein Award (1954) and Lawrence Award (1962). He is known to be one of the greatest scientific geniuses of the 20th century.

The vision of manufacturing nanoscale machines by Richard Feynman was taken to the next higher level by Eric Drexler, who proposed the idea of fabricating a nanoscale *assembler*, which would be able to replicate itself and other objects of arbitrary complexity. The new technology, handling individual atoms and molecules with precise control to build nanostructures (nanomachines or nanocircuits), is called *molecular nanotechnology.* Both the terms, 'molecular technology' and 'nanotechnology', are in use quite interchangeably. His work on molecular technology done at MIT, resulted in his book *Engines of Creation: The Coming Era of Nanotechnology*, published in 1986. His work was criticized by none other than the Nobel Prize winner Richard Smalley, who argued that the 'fat' claims of Drexler on molecular nanotechnology were 'impossible' to achieve. On the other hand, Ray Kurzweil supported Drexler's ideas as being practical and even happening, already. Undeterred by the criticism for his predictions about the success of molecular nanotechnology, Drexler, in one of his speeches, quoted Gandhi on critics 'First they ignore you. Then they laugh at you. Then they attack you. Then you win,' displaying his optimism and confidence in the future prospects for atomically precise manufacturing technology.

Kim Eric Drexler (1955)

Kim Eric Drexler was born in Almeda, California. He holds all his academic degrees from MIT. He received his B S in Interdisciplinary Sciences in 1977, M S in Astro/Aerospace Engineering with a thesis titled *Design of High Performance Solar Sail System* in 1977, and Ph D in Molecular Nanotechnology with thesis entitled *Molecular Machinery and Manufacturing with Applications to Computation* in 1992. The same year, his Ph D thesis was published as *Nanosystems: Molecular Machinery, Manufacturing and Computation*, which received the Best Computer Science award in 1992 from the Association of American Publishers.

Inspired by the vision of Richard Feynman, Drexler studied the principles of productive nanosystems—nanomachines used to make products with atomic precision called *assemblers*. Drexler and Christine Peterson (his wife at that time) founded the Foresight Institute in 1986 to promote their mission of 'Preparing for Nanotechnology'. He is a staunch advocate for nanotechnology, believing firmly in the great prospects and potential of nanotechnology, never worrying about his critics. He introduced the concepts of molecular nanotechnology to a wider scientific community through his research publications, books, popular talks, and is regarded as the founding architect of the field. As a consultant, he advises on how the current research can be directed more effectively towards high investment returns. Currently, he is an Academic Visitor at Oxford University.

Eric Drexler resides in Oxford (UK) with his wife Rosa Wang.

1.5 NATURE—THE SUPREME GURU

Man always wonders at the mysterious ways in which nature works. Since time immemorial, he has been trying to understand mother nature in order to discover her laws and invent new things to fulfil his necessities. Using all skills and resources at his command, man makes a semblance of an attempt at mimicking nature in creating life in the laboratory or building computers with human brain-like functions, which is still but a pipe dream. Even though recent progress in science and technology has been very impressive, with the achievement of great feats such as the landing of man on the moon in 1969, landing the *Curiosity* rover on Mars in 2013, or the *Mangalyaan* mission entering Mars' orbit in its maiden attempt in 2014, man is still nowhere close to matching nature's intelligence and the ways in which nature works. The human approaches and attempts at solving the basic worldly problems, with respect to garnering the energy resources, water management, alleviation of hunger, protection of the environment, control of diseases, and so on, is at best, primitive. There is still a lot more to learn from mother nature.

Most of the processes occurring in nature are highly efficient, work at atomic and molecular levels, and build larger structures atom-by-atom in a process known as the 'bottom-up' approach. For example, nature's processes, such as photosynthesis in storing solar energy, cycling oxygen and removal of CO_2 from the atmosphere, and 'water cycle' in purification and distribution of water all over the earth, are not only highly efficient, but also maintain an environmental equilibrium, which is critical for the survival of life on our planet. The efficiency of man-made devices and systems is in general, quite low. For example, the efficiency is ~25% for the combustion engine of a motorcar. In case of photovoltaic solar cells, it is 10% for amorphous Si, 15–25% for a single crystalline Si, and ~30% for GaAs-based devices. In addition, photovoltaic solar cells are not cost-effective, when compared to the energy obtained from fossil fuels.

The human brain is a sample of nature's grandeur. An average human brain is a network of more than 100 billion nerve cells called *neurons* and they all do their jobs simultaneously. Each neuron may be connected to 1000–10,000 other neurons. They send signals chemically and electrically through molecular neuro-transmitters and receptors (nanos), across 1000 trillion synaptic connections, which is equivalent to a trillion bits per second microprocessor. The estimated memory capacity of the human brain varies in the range of 1–1000 terabytes, as compared to a total of 10 terabytes data representing 19 million volumes of the US Library of Congress. The electronic computers work in vastly different ways. A computer follows steps, one at a time, but it can do each one of them incredibly fast. Parallel networking in computing is also employed in the present-day computers, but only to a limited scale as compared to the human brain. No computer has been made by man matching the capacity and complexity of the human brain. Even the most modern computers cannot match the sheer capability or capacity of the human brain.

1.6 EXISTENCE OF NANOSTRUCTURES IN NATURE

There is a vast expanse of matter in nature comprising our planet earth, solar system, galaxy, and beyond, all through the universe. As we know, matter was created after the *Big Bang*, from the conversion of energy radiation into subatomic particles, atoms, molecules, gases, solids, and all the other forms of matter or antimatter. Thus, the whole creation has come into existence by the mechanism that operates using a 'bottom-up' approach, starting with the most subtle form of matter. The creation of smaller objects from larger bodies is a natural corollary of 'bottom-up' approach, that is, 'top-down' is also possible in nature. We will discuss here a few examples of biological nanostructures found around us on the earth and an example of the presence of nanoparticles deep in the interstellar space.

1.6.1 Biological Nanostructures

Living organisms are built of cells, which are microscopic in size, typically 10 μm across. The cell parts, however, are in the submicron regime, and some of them, like proteins, are with a typical size of about 5 nm, lying on the lower side of the nanoscale. A real bone is a nanocomposite of inorganic hydroxyapatite crystallites dispersed in the organic matrix, which is mainly composed of collagen. Due to this type of structure, the bone is mechanically tough and, at the same time, plastic, so that it can recover from mechanical damage. The collagen, being an elastic protein, improves fracture resistance and imparts elasticity to the bone and forms bundles of elongated tissue fibrils that are 80–100 nm in diameter; whereas the inorganic part, essentially comprising mineral calcium phosphate, provides rigidity to the bone.

A sea creature, called *abalone* belonging to a variety of marine snails, is known for its exceptionally strong shell used as a protection shield to hide inside when threatened. It creates the shell using calcium carbonate from the saline sea water to form nanostructured tiles glued together by a mixture of carbohydrate and protein. Abalone shell is an illustration of the strength of nanocomposite materials found in the nature. Marine unicellular cyanobacteria have evolved a unique type of swimming motility with the help of nano-sized flagella or motor-organs. The bacteria can orient themselves along the earth's magnetic field lines and navigate towards the optimal concentration of nutrients using magnetic mineral nanocrystals enveloped in a membrane and arranged in linear chains along the bacterium cell. Dragline silk is yet another example of natural fibrous protein spun by spider. Spiders secrete proteins dissolved in water-based solvents through long fine ducts leading to microscopic spinners, which wind the several strands together forming fibrous silk. Spider silk exhibits a unique combination of incredibly high tensile strength and ductility, comparable to or even several times stronger than high-grade alloy steel. Description of different biological nanostructures is given in Chapter 11.

1.6.2 Discovery of Buckyball

The scientists were investigating the existence of small particles of matter present in the interstellar dust between the stars and galaxies in the region of outer space. It was observed that when the light from far-off stars reaches the earth after traversing through such dust, an absorption peak appeared in the spectrum at 220 nm (5.6 eV). This absorption peak was attributed to small particles of graphite. While trying to study the carbon-rich grains found in the dust expelled by old stars in the outer space, Harold Kroto from University of

Sussex found evidence of long, linear chain molecules of carbon. He wanted to create such molecules in the laboratory by evaporating graphite using high-power lasers to investigate their structures in detail. He contacted Richard Smalley from Rice University in Houston, who was having an experimental setup in his laboratory to make small clusters of atoms using high-power pulse lasers. When the experiment was conducted by evaporating graphite into small grains, the mass spectroscopic analysis yielded a surprising result of 720—mass consisting of 60 atoms of carbon, each of mass 12. Thus, the collaboration resulted in the discovery of C_{60} molecule, which is the third allotropic form of carbon besides graphite and diamond. The C_{60} structure has 12 pentagonal and 20 hexagonal faces symmetrically arranged to form a ball-like molecule, as shown in Fig. 1.6. Since the shape of the molecule reminded Smalley of the geodesic dome designed by Buckminister Fuller, he named the C_{60} molecule as 'buckministerfullerene' or simply *fullerene*. The most spherical, novel molecule ever discovered was nicknamed the *buckyball*. For this discovery, Kroto, Curl Jr, and Smalley shared the Nobel Prize for Chemistry in 1996.

Fullerenes (buckyballs) are extremely strong molecules with hardness similar to or greater than diamonds. The sheer strength of fullerenes makes them potential candidates for applications in composite materials, coatings for wear-resistance surfaces, as components in scientific instruments such as electron probe microscopes, and as an exceptional lubricant material. The high electron affinity and superior ability in charge transport makes them suitable for applications such as organic bulk heterojunction solar cells, which are flexible and can be rolled up or spread over any surface. The fullerene may also find application in hydrogen gas storage because they can be hydrogenated and de-hydrogenated, reversibly. The properties of fullerenes can be changed through modification by adding or substituting an atom, a process called *functionalization*, and can be used for targeted drug delivery. They have the potential to find numerous other applications, such as sensors.

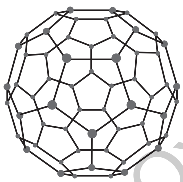


FIG. 1.6 C_{60} molecule showing 12 pentagonal and 20 hexagonal faces

1.7 NANOMATERIALS USED PRIOR TO 1990s

The words nanoparticles, nanomaterials, or nanostructures, together with the related concepts, came into frequent use in the early 1990s. However, the use of various such materials by humanity could go back to thousands of years in the past. The use of *kajal* (in Hindi) or *kohl* (in Arabic) as eye cosmetics has been prevalent in North Africa, Middle East, South Asia, and maybe in other parts of world from ca. 3100 BC. In India, it is prepared by women of households from the soot of a lamp burning edible oil (mustard, coconut, etc.) by holding an earthen pot above the flame at night. Collecting the lamp-black in the morning and mixing it with *ghee* (cow's butter) makes the eye-black ready for use. As the particle size of carbon black thus obtained is very very fine (nano-size), the application around the eyeballs makes their movement smooth and gives a cooling sensation. Another version of the Ayurvedic eye ointment called *ragda* or *ragra* (in Hindi, meaning an end product obtained on grinding), perhaps an adaptation of the original *kohl* from ancient Egypt, is traditionally prepared in the form of a very fine thin paste obtained by grinding a mixture of galena (PbS) /stibnite (SbS), Ayurvedic herbs, silver, gold, or copper metal, and other ingredients for long periods, and used as medicine for curing eye-ailments. As silver and gold particles have antibacterial properties, they provide relief from eye conjunctivitis and other bacterial infections. Very thin foils called *vark* (in Hindi) composed of pure metal (~99.9%), typically silver or gold, are used for garnishing sweets, betel nuts and leaves, and fruits in South Asian cuisine. Being antibacterial, the minuscule quantity of silver is orally administered or chewed by people with these food preparations for medicinal effects.

Famous for his invention of the laws of electromagnetic induction that powers the electric motors and generators, Michael Faraday also discovered the laws of electrolysis and formed colloids of gold, presently known as nanoparticles, way back in 1856. German bacteriologist Robert Koch discovered in 1860 that the tubercle bacillus could not survive in the presence of colloidal gold and silver. Koch was awarded the Nobel Prize for Physiology or Medicine in 1905 for his inventions and discoveries in relation to tuberculosis. Colloidal gold is also believed to be a remedy for chronic inflammation, depression, and several other diseases. Silver in the colloidal form is also considered as a powerful natural antibiotic, used for thousands of years in the treatment of several diseases and having no side effects.

Gold colloids are incorporated in a glass matrix to produce different hues of coloured glasses depending on the size of the colloidal particles. These tainted coloured glasses are used in flower vases and window panes for decorative purposes, particularly, in churches all over the world. The dependence of scattering of light at different wavelengths by small particles, on their sizes, was formulated by Gustav Mie, known after him as *Mie's theory* [Mie 1908]. The theory describes the colour effects connected with colloidal gold particles through solving the Maxwell equations for interaction of electromagnetic radiation with small particles. Mie observed and successfully explained the colour of gold colloids changing with the diameter of the gold spheres [Bohren et al. 1983]. As the scattering of light of different wavelengths is a function of particle size, glasses of different colours can be realized by varying the metal particle size in the glass. A good illustration of the particle-size effect on light scattering is seen in the Lycurgus Cup, called the *cage cup*. Designed and produced by the ancient Roman glass industry, sometime in 4th century AD, it is preserved and displayed in the British Museum, carrying the legend of King Lycurgus. Containing silver and gold nanoparticles of about 70 nm across, dispersed in the colloidal form throughout its dichroic glass, the cup appears red in the transmitted light and green in the reflected light.

1.8 PROSPECTS AND POTENTIAL OF NANOTECHNOLOGY

It can be said that almost every 50 years, there is a great invention taking place in the history of science and technology. First, it was the development of the vacuum tube in the late 19th/early 20th century, which dominated in its applications in electronic communication, computers, and consumer electronics for more than half of the 20th century. Then, it was the invention of semiconductor transistors in 1947, a solid-state version of the vacuum tube triode, which revolutionized the world of electronics and led to the onset of the information age. The invention of the transistor has brought advancement in technology to a level beyond imagination, making satellite, internet, and mobile communication possible. The computers have passed through several incarnations from the mainframes using vacuum tubes, occupying a huge space and consuming several tens of kilowatt energy, to the desk-, lap-, and palm-tops, and supercomputers; and now we have smart phones and tablets with numerous applications.

In the late 1980s, it was the advent of yet another great technology called nanotechnology, having tremendous prospects and potential, which did not go unnoticed by any developed or developing countries alike, around the world. Countries such as the US, Japan, China, and Europe spend billions of dollars in funding nanotechnology-related projects. Even developing countries put their scarce resources to fund for research and development in nanotechnology. For example, India launched an ambitious programme in 2007 on nanoscience and technology called *Nano Mission* with an allocation of US$ 250 million for five years. The total funding in India for basic research and development in the field of nanoscience and technology, including joint collaborations, is US$ 671.51 million, which still remains one of the lowest, according to global standards [7th Bangalore Nano India 2014]. It has been estimated that the market will grow to over US$ one trillion by 2015.

The prospects and potential applications of nanotechnology encompassing all fields of human endeavour such as energy, information and communication, environment, industry, defence, agriculture, textiles, and other household consumer goods are discussed in detail in Chapter 14.

SUMMARY

- The word ‘nano’ is derived from the Greek word *nanos* or Latin word *nanus*, meaning ‘dwarf’ and qualifies objects of matter having at least one physical dimension in the range 1–100 nanometres, as nanomaterials or nanostructures. A nanometre stands for one billionth of a metre, that is, 10^{-9} m or 1 nm.
- Macroscopic scale refers to the large objects visible to the unaided, naked eye. The lower size limit of these objects visible to the naked eye is around 10 micron.
- Objects that are smaller in size than the eye’s visibility limit and that require a microscope to detect or observe them, down to individual atoms, fall on the microscopic scale, which also encompasses the nanoscale. Today, electron microscopes are capable of imaging even individual atoms.
- Nanoscience and technology cuts across all disciplines and is truly a multi-disciplinary subject. Nanotechnology deals in employing nanostructures to develop products with possible practical applications.

- The invention of the vacuum tube, an active component of electronic circuits, was critical to the growth of electronics and communication and was the first major landmark in the history of electronics. The vacuum tube dominated in its application in electronics communication, computers, and consumer electronics for more than half of the 20th century.
- J.C. Bose developed the first solid-state galena detector, a forerunner of modern semiconductor mm-wave diode detectors, for reception of millimetre waves at 60 KHz in 1901.
- Theoretical advances in quantum mechanics were behind the development of quantum theory of solids, which played a critical role in the understanding and development of materials and invention of several semiconductor devices, including the transistor—the biggest invention of the 20th century.
- Recent origin of nanoscience and technology can be traced back to the predictions made by Richard P. Feynman in his visionary and prophetic talk 'There is plenty of room at the bottom'. Many of his predictions have come true.
- The vision of manufacturing nanoscale machines by Feynman was taken to a step further by Eric Drexler, who proposed the idea of fabricating a nanoscale assembler. An assembler would be able to replicate itself or other objects of arbitrary complexity. The new technology, with capability to handle individual atoms and molecules with precise control to build nanostructures, nanomachines, or nanocircuits, is termed as molecular nanotechnology.
- Nanomaterials and devices obey the laws of quantum mechanics and occupy discrete energy states like atoms and molecules.
- Living organisms are built of cells, which are microscopic in size typically 10 μm across. The parts of the cell are, however, in the submicron regime and some of them, such as proteins with a typical size of about 5 nm, lie on the lower end of the nanometre scale.
- The words nanoparticles, nanomaterials, or nanostructures, together with the related concepts, came into frequent use in the early 1990s. However, the use of various such materials by humanity goes back to thousands of years in the past.
- In the past, three great inventions have been made in the history of science almost every 50 years. First, it was the development of the vacuum tube in the late 19th/early 20th century, forming a vital component of circuits, computers, and radio communication systems. The development of semiconductor transistor in 1947 was perhaps the greatest invention of 20th century, a solid-state version of the vacuum tube. The solid-state transistor did revolutionize electronics, leading to the onset of the information age. Then in the late 1980s, it was the advent of yet another great technology called nanotechnology, which offers tremendous prospects and potential to bring about remarkable changes to the different facets of life on Earth, in the times to come.
- The strength of fullerenes (buckyballs) makes them potential candidates for applications in composite materials, coatings for wear-resistance surfaces, as components in scientific instruments, and an exceptional lubricant material. Due to their high electron affinity and superior ability in charge transport, fullerenes are also considered as suitable for use in organic solar cells, hydrogen gas storage, and sensor applications.
- The properties of fullerenes can be changed through modification by adding or substituting an atom, a process called functionalization, which can be used for targeted drug delivery.

KEY TERMS

Integrated circuits When a circuit with several components, such as diodes, transistors, resistors, and the interconnects are built on a single crystalline semiconductor substrate/wafer, it is called an integrated circuit (IC).
Molecular nanotechnology The technology related to building nanostructures, which involves handling of atoms and molecules with precise control is called molecular nanotechnology.
Nanoparticles/Nanostructures Particles, objects, or devices with size in the range 0.1–100 nm are called nanostructures or nanoparticles.
Nanoscale Scale of length that is used in measurement and characterization of nanoparticles in units of 10^{-9} m or nm spanning the range 0.1–100 nm.
Quantum Light consists of tiny packets of energy called quanta with energy $E = h\nu$, where h is the Planck's universal constant 6.63 × 10^{-34} J.s and ν is the frequency of the light (electromagnetic) wave.
Quantum/wave mechanics The branch of mechanics that describes the motion and interaction of subatomic particles, atoms, molecules, and other small objects such as atomic clusters or nanoparticles. Quantum mechanics incorporates the concepts of quantization of energy, the wave–particle duality, the uncertainty principle, and the correspondence principle.

EXERCISES

REVIEW QUESTIONS

1.1 Define nanoscale and give a few examples of nanomaterials—living/non-living.
1.2 Differentiate among nano, microscopic, and macroscopic objects by giving examples for each of them.
1.3 Give a brief account of the historic perspectives of nanotechnology.
1.4 Justify the statement, 'Nanotechnology is truly a multidisciplinary subject'.
1.5 Who made the statement, 'There is plenty of room at the bottom' and what was his big vision for the small world?
1.6 Who coined the term 'molecular nanotechnology'?
1.7 Why is it said that nature is the Supreme Guru?
1.8 Give a few examples of the existence of nanostructures in nature.
1.9 Describe briefly the use of nanomaterials prior to the 1990s.

NUMERICAL PROBLEMS

1.1 If a solid cube with one cm side is divided into nano-size tiny cubes with 10 nm side, calculate the surface-to-volume ratio R (S/V m^{-1}) for the total material in two cases. Draw an appropriate conclusion about the change in R when the bulk material is converted into nanoparticles.
1.2 Density of Ge crystal is 5.35 g/cm^3 and its atomic weight is 72.63. Calculate the radius of a Ge atom using this data. Assume the packing fraction of a diamond-like Ge crystal structure to be 0.34, which is the fraction of the volume occupied by the atoms, leaving a vacant space in the remaining fraction 0.66.

MULTIPLE-CHOICE QUESTIONS

1.1 The transistor was invented in the year
(a) 1885 (b) 1962 (c) 1989 (d) 1947
1.2 Who invented the transistor?
(a) Michael Faraday (b) S.N. Bose
(c) William Shockley, John Bardeen, and Walter Brattain (d) Eric Drexler

1.3 Which of the following sizes of objects lie on the nanoscale?
(a) 1.7 m (b) 10^{-5} m (c) 50×10^{-9} m (d) 1×10^{-6} m (e) 10 m
(f) 1×10^{-9} m

FILL IN THE BLANKS

1.1 The word 'nano' is derived from the Greek word '___________' or Latin word '___________', meaning 'dwarf'.
1.2 The emergence of nanotechnology is based on the fundamentals of ___________ and other ___________ advances in the last hundred years or more, prior to the inception of nanotechnology.
1.3 Vacuum tubes perform basic functions of ___________.
1.4 ___________ is a sample of nature's grandeur.
1.5 Living organisms are built of ___________, which are ___________ in size, typically 10 μm across.

MATCH THE FOLLOWING

1.1 Nanometre scale	(a) Size of red blood cells
1.2 Micrometre scale	(b) Human hair
1.3 Macrometre scale	(c) Virus

ANSWERS

NUMERICAL PROBLEMS

1.1 Surface-to-volume ratio *R* increases by 1×10^6 times on dividing the cube into nanoparticles of 10 nm side cubes. One may conclude that the nanoparticles have a characteristically large surface-to-volume ratio when compared to bulk materials.
1.2 Radius of a Ge atom is 4.28 Å.

MULTIPLE-CHOICE QUESTIONS

1.1 (d) 1.2 (c) 1.3 (c), (f)

FILL IN THE BLANKS

1.1 nanos, nanus 1.2 quantum mechanics, scientific and technology
1.3 rectification, amplification, switching, and mixing 1.4 human brain
1.5 cells, microscopic

MATCH THE FOLLOWING

1.1 (c) 1.2 (a) 1.3 (b)

REFERENCES

'1947—Invention of the Point-contact Transistor', http://www.computerhistory.org/semiconductor/timeline/ 1947-Invention.html, last accessed on 18 May 2014.

7th Bangalore INDIA NANO, 'Report - Creating Growth Opportunities for Indian Nanoscience and Nanotechnology', Dec. 5–6 2014: http://www.bangaloreindianano.in/pdf/Report-Creating-growth-opportunities-Indian-nanoscience-nanotechnology.pdf, last accessed on 20 May 2015.

Bohren, C.F. and Huffman, D.R., *Absorption and Scattering of Light by Small Particles*, John Wiley & Sons, New York (1983).
Bose, Jagadis Chunder, *Detector for Electrical Disturbances Patent*, US Patent No. 755840 (1904).
Bose, J.C., *Collected Physical Papers*, Longmans, Green & Co., New York (1927).
Brinkman, W.F., Haggan, D.E., and Troutman, W.W., 'A History of the Invention of the Transistor and Where It Will Lead Us', *IEEE J. Solid-state Circuits*, **32**, pp. 1858–1865 (1997).
Dacey, G.C. and Ross, I.M., 'Unipolar Field-effect Transistor', *Proc. IRE*, **41**, pp. 970–979 (1953).
Emerson, D.T., 'The Work of Jagadis Chander Bose: 100 Years of MM Wave Research', *IEEE Trans. Microwave Theory and Research*, **45**, pp. 2267–2273 (1997).
Hilsch, H.R. and Pohl, R.W., 'Control of Electron Current with a 3-electrode Crystal and as a Model of a Blocking Layer', *Zeits. für Physik*, Vol. **3**, pp. 399–408 (1938).
http://www.quantumbalancing/news/cs_universal.htm
IEEE History Center, 'Nikola Tesla: 1856–1943' (2003).
Kahng, D. and Attala, M.M., 'Silicon–silicon Dioxide Field Induced Surface Device', presented at Solid State Research Conference, Pittsburg, PA, June 1960.
Lilianfeld, Julius, *Method and Apparatus for Electric Current*, US. Patent No. 1745175 (1926). Filed Oct. 8 1926, issued 18 Jan 1930.
Mie, Gustav, 'Contributions on the Optics of Turbid Media, particularly Colloidal Metal Solutions', *Ann. Phys.,* **25**, pp. 377–445 (1908).
Moore, Gordon, 'Cramming More Components Onto Integrated Circuits', *Electronics*, Vol. **38**, No. 8 Apr 1965.
Pfann, William G., *Continuous Zone Refining Using Cross-Flow*, US Patent No. 2926075A (1960).
Planck, Max, 'On the Law of Distribution of Energy in the Normal Spectrum', *Ann. d. Phys.*, **4**, 553 (1901).
Scaff, J.H., Theurer, and Schumacher, 'P-type and N-type Silicon and Formation of Photovoltaic Barrier in Silicon Ingots', *Trans. A.I.M.E.*, **185**, pp. 383–388 (1949).
Sengupta, D.L., Sarkar, T.K., and Sen, D., *Proc. IEEE*, **86**, pp. 235–243 (1998).
Wanlass, F.M. and Sah, C.T., 'Nanowatt Logic Using Field Effect Metal-oxide Semiconductor Triode', *Proc. Intl. Solid State Circuits Conf.*, pp. 32–33 (1963).
www.britishmuseum.org, last accessed on 18 May 2015.
www.epa.gov/rpdweb00/docs/cleanup/.../chapter-2-carbon-nanotubes.pdf, last accessed on 15 May 2014.
www.nobelprize.com, last accessed on 18 May 2015.