Fundamentals of Solid State Engineering

Manijeh Razeghi

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Fourth Edition

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Foreword

Students commonly think of a textbook as merely a tool to get prepared for exams. This is not the right way of looking at it! A textbook is the fruit of long-term studies and experience acquired by the author and reflects her or his personality. It embodies priorities, knowledge, and I dare say even dreams and life attitudes. Compare the difference in style and content in the now classic physics textbooks by Landau and Feynman. Both Landau and Feynman were scientists whose minds were ready to listen to the music of the heavens. But how very differently! Landau wrote with the authority of a Zeus and his book sounds like the ultimate message from Heaven, while Feynman's style is more modest, and his curiosity and quest for truth could hardly be matched by anyone. His famous textbook is like an invitation to travel through the Disneyland of Nature, where he acts as a guide, but a guide who is also learning during this journey. And there is a third example: the Chicago lecture notes on quantum mechanics by another Nobel laureate – Enrico Fermi. At first sight, it appears to be more student friendly, simple, and very much to the point, but what a simplistic and, indeed, incorrect interpretation that would be! Fermi made a selection of topics and then reduced the content to the absolute essence of what has to be understood to get prepared for a journey into the quantum wonderland. He did it in such a way that an average student had the impression he or she understood everything, while a more demanding student would get a sense of much more: a feeling that a miraculous quantum world was waiting for him behind invisible doors, full of questions and surprises. Fermi did what Albert Einstein once said about science in his peculiar English – *do it simple, but not simpler*.

I admire this textbook by Professor Razeghi as much as I respect her research achievements, which she fulfilled in her personal journey through this demanding life. She was born in Persia, but left her motherland forever to join her new country France, the country that gave her the chance to continue the science she loved so much. In doing so, she followed the footsteps of Marie Curie, who a century before left oppressed Poland as a young math teacher by the name of Skłodowska. Welcomed in France, Skłodowska completed her studies at the Sorbonne, got married to a brilliant French physicist Pierre Curie, and then spent endless hours working with him, processing tons of radioactive ores from Czechoslovakia. Together they eventually extracted small grains of the miraculous polonium and radium – two radioactive elements they discovered and named. This superb

technological achievement, of which Marie definitely was the master and the *spiritus movens*, opened new avenues for science and finally led her twice to Stockholm to be awarded the Nobel medal.

Dr. Razeghi hopefully was not forced to work in a cold and primitive warehouse, like the Curies had to. The wise management of the French electronic giant Thomson spotted her unique talents and gave her proper resources to realize her visions and dreams. In a short time she became the First Lady in solid-state physics and made Thomson the leader in modern III-V compound semiconductor technology. Her laboratory was a dream for most of us, well before the common excellence of today in many places. But Razeghi became a technologist by choice. She was driven by the vision of the ultimate device backed by a deep understanding of the science and full of curiosity. This is what guided her. No wonder she became a very desired collaborator for top labs and personalities in the semiconductor world. She soon reached the peak of the Himalayas and could well have stopped there. But not for Mme Razeghi. After many years of success, she left friendly Europe for the next grand tour of her life, to the host of the most advanced materials science – the United States – interestingly, not to another industrial super-organization like Thomson, but to a university, where she could share her experiences and shape the next generations. Her energy and visions attracted money, and the money helped to create one of the most advanced university-based semiconductor labs in the world, visited and applauded by most Nobel laureates in the field.

So, dear readers, make sure that you learn from this book, but not only science and technology, which is presented with great clarity, skill, and care (there is even an appendix on how to work with dangerous chemicals in the MOCVD lab!). Maybe you will hear – just as I did – the whisper of the modestly hidden powerful message from Professor Razeghi: *the only thing to prevent you from performing miracles in the tournament with Nature is yourself*. To win and to have pleasure, learn first, then practice in the lab, and work with your notebook. If you work hard enough and still enjoy it, you may have the stuff for the ultimate destiny – real Himalayas – the discourse with nature: understand her laws and limitations, but also her immense and endless frontiers.

Thank you Manijeh for the guidance.

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Preface

Learning from Nature: Structure of Matter – Atoms

Nature is the best innovator and teacher. Scientists know for a while now that all matter consists of atoms. The atom is the smallest part of any material element. So when we look around us and observe the material world, we know that these natural colors we see are the light emitted by atoms. But atoms consist of nuclei surrounded by clouds of electron and the light particles they emit are what we call the quanta of light or photons. At the end of the last century, we learned from the great physicist James Clerk Maxwell that light, and its individual quanta, the photons are electromagnetic waves emanating from atomic emission or more generally from oscillating charges. Electrons undergo a transition from a higher to a lower orbit in an atom that emits light and conversely can also absorb light. The detail of this transition determines the energy or wavelength of the light. This includes the entire spectrum of light from gamma rays to UV to visible and to the invisible infrared (IR) rays down to the THz. Our eyes can see only a small part of the total photonic spectrum, from 300 to 700 nm in wavelength. So it is understandable that one of the first and primary aims of physicists was to try making instrumentation in order to see the rest of the spectrum as well, using artificial eyes. These electronic eyes are made by materials engineering. Indeed this has been achieved now to a great extent, and the progress is so important that artificial eyes covering a much larger range of photonic energies are being made and are constantly being improved. This progress was acquired by first developing a deep understanding of the workings of atoms. In fact one can say that the last century was the century of exploring the atom and mastering the science of materials. The next century will be the century of genes and biological cells.

Physicists have discovered that detecting and creating photons of different wavelengths require first a profound understanding of the atom, and this has been made possible by the science of quantum mechanics. The second step was to investigate a very special type of materials called the semiconductors. The science of semiconductors is central to all modern device physics, including the electronic chip and computer. Unlike in metals, electrical charges in semiconductors are not free to move under the action of a small electric field; they first have to be "excited,"
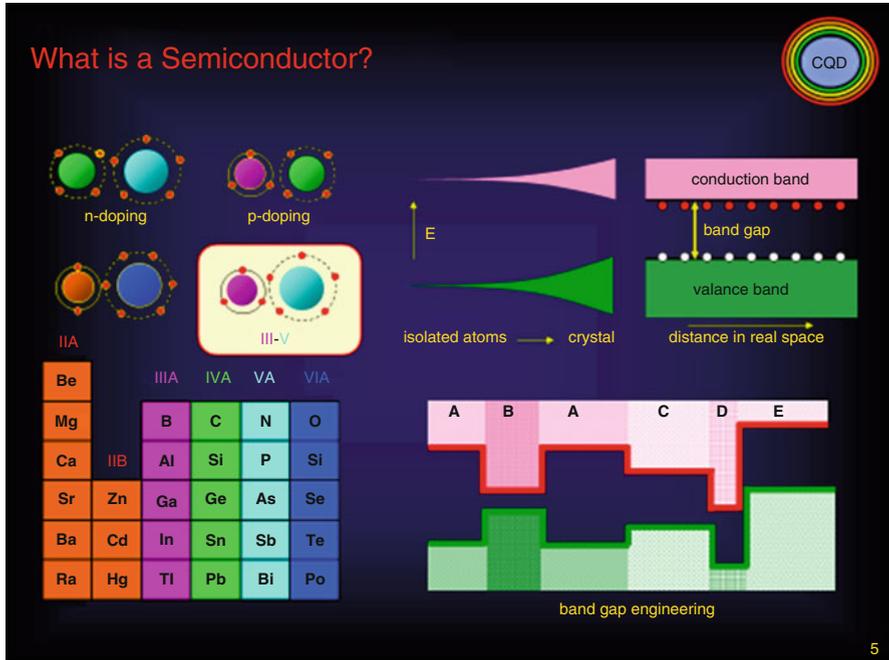
Fig. 1 Basic elements used to make pure and compound semiconductors; each has its own bandgap and, when combined into compounds, develops a new bandgap; layer-by-layer deposition generates new class of semiconductor superlattices with designer bandgaps (bottom right)

for example, by light or heat, to cross the energy gap formed by the bonding structure. This gap determines the sensitivity of the material to a particular wavelength and varies according to semiconductor type, and indeed the gap can now mostly be designed. To design and understand semiconductors, one has to realize that semiconductors, like other materials, consist of different types of atoms bonded together. Materials can be liquid, soft, or hard, and here we are in the first place talking about hard solids. The most useful and well-known semiconductors are in the category of silicon and germanium. What distinguishes them is that each atom has four valence electrons which combine their orbits to point to four different directions of space (tetrahedron) where they overlap and bond with four corresponding neighbor orbitals. These form semiconductors of the group IV-IV elements. Semiconductors can also be formed by combining group III and V elements such a GaAs or InAs (see Fig. 1). Here we have three and five valence electrons in the outer shells, respectively, and bonding comes about by first transferring an electron from element five to three, making it possible to form as in silicon, four tetrahedral bonds. There are many examples of III-V compounds, and they are extremely important to technology. Similarly, one can combine semiconductors by combining II-VI elements (CdTe, CdSe) where now two electrons are transferred from VI to II, making it again 4-4 bonds. A particularly inspiring and special atom is the atom of
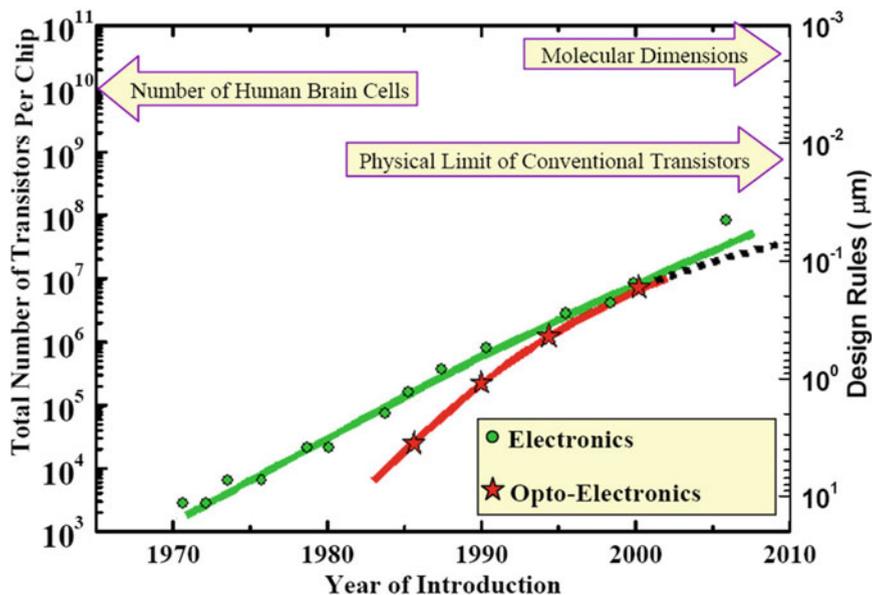
Fig. 2 Evolution of the total number of transistors per computer chip and their corresponding dimensions (in an inverted scale) as a function of year. For comparison, the number of human brain cells is shown on the left scale. In addition, the physical dimension limit for conventional transistors and the size of molecules are shown on the right scale

the element carbon. The four valence electrons of carbon can bond with one, two, or three neighbors and in this way form organic molecules, polymer chains, or two- or three-dimensional solids. A notable example is diamond which is bonded in three dimensions and is a high bandgap semiconductor with the highest thermal conductivity and hardness. The next example is the two-dimensional graphene (G). Graphene is causing a revolution in applied sciences. Carbon physics has already led to the awarding of three Nobel prizes, one for buckyballs (fullerenes) and the other two for graphene.

By now the reader should get a feeling of how exciting and useful solids and semiconductors and their applications are. But before we get into the details of how the solids work, what constitutes the important physics and engineering, and how we can develop the necessary sensory tools (see Fig. 2), let us revisit our own natural sensory systems and find out what challenge we are facing when we want to imitate or surpass nature.

Nature has stimulated human thought and invention before recorded time. Controlled fire, the wheel, and stone tools were all undoubtedly "invented" by humans, who drew inspiration from some natural phenomena in our prehistory, such as a wildfire created by a lightning strike, the rolling of round boulders down a steep hill, and perhaps wounds caused by the sharp rocks of a river bottom. There are examples during recorded times of other such ingenuity inspired by nature. Sir Isaac Newton

wrote that seeing an apple fall from a tree outside his window provoked his initial thoughts on the theory of gravitation. The Wright brothers and countless unsuccessful aviators before them were stimulated by the flight of birds. Similarly, we can look to nature to give us inspiration for new electronic devices.

Even a casual glance at the living world around us reveals the rich diversity and complexity of life on Earth. For instance, we can choose virtually any organism and demonstrate that it has the ability to sense and react to the surrounding world. Over millions of years of evolution, almost all types of life have developed some type of detection ability, seamlessly integrated into the other functions of the life form. More specifically, we can examine the basic human senses of hearing, smell, taste, touch, and sight to inspire us to understand more about the physical world.

Human hearing is based around the organ of Corti, which transduces pressure waves created within the fluids of the cochlea. The 20,000 micron-sized hair cells not only convert these waves into electrical impulses and transmit them to the brain via the auditory nerve but allow audio spectral differentiation depending on their position within the organ. Typical human frequency response ranges from 20 kHz to 30 Hz with sensitivity up to 130 decibels. Drawing from this natural example, today microphone manufacturers produce tiny transducers with dimensions of a few hundred microns.

The human sense of smell is based around approximately twelve million receptor cells in the nose. Each cell contains between 500 and 1000 receptor proteins that detect different scents and relay the information to the olfactory bulb and onto the brain. Today, researchers are developing "electronic noses" to mimic and improve upon the human olfactory system. Important applications include the detection of explosives as well as toxic chemicals and bio-warfare agents.

Gustatory receptors on the human tongue act as detectors for specific chemical molecules and are the basis for the sense of taste. Between 30,000 and 50,000 individual taste receptors make up the taste buds that cover the tongue and are capable of sensing bitter, sour, sweet, salty, and monosodium glutamate (MSG)-based foods. "Artificial tongues" are being developed to similarly classify flavors and also to perform specialized chemical analysis of a variety of substances. Aside from the obvious commercial applications (such as active sampling of foods and beverages in production), these devices may act in conjunction with "electronic noses" to detect various chemical agents for security purposes.

The sense of touch in humans allows several detection mechanisms, including specific receptors for heat, cold, pain, and pressure. These receptors are located in the dermis and epidermis layers of the skin and include specialized neurons that transmit electric impulses to the brain. Today, microswitches have been developed to detect very small forces at the end of their arms much like the whiskers of a cat. Thermocouples have been developed for sensitive temperature detection, and load cells are used for quantitative pressure sensing.

The sense of sight is perhaps the most notable form of human ability. Micron-sized rods and cones containing photosensitive pigments are located in the back of the eye. When light within the visible spectrum strikes these cells, nerves are fired and the impulses are transmitted through the optic nerve to the brain, with electrical

signals of only 100 mV between intracellular membranes. With the proper time to adapt to dark conditions, the human eye is capable of sensing at extremely low light levels (virtually down to single-photon sensitivity). However, our vision is limited to a spectral band of wavelengths between about 400 and 750 nanometers. In order to extend our sensing capabilities into the infrared and ultraviolet, much research has gone into exploring various material systems and methods to detect these wavelengths.

In order to improve and stretch the limits of innate human capabilities, researchers have mimicked nature with the development of quantum sensing techniques. Using these electronic noses, tongues, pressure sensors, and "eyes," scientists not only achieve a better understanding of nature and the world around them but also can improve the quality of life for humans. People directly benefit in a number of different ways from these advances ranging from restoration of sight, reduction in terrorist threats, and enhanced efficiency and speed of industrial processes.

Beyond human sensing capabilities, we can also look to the brain as an example of a computing and processing system. It is responsible for the management of the many sensory inputs as well as the interpretation of these data. Today's computers do a good job of processing numbers and are becoming indispensable in our daily lives, but they still do not have the powerful capabilities of the human brain. For example, state-of-the-art low power computer processors consume more power than a human brain while having orders of magnitude fewer transistors than the number of brain cells in a human brain (Fig. 1). Forecasts show that the current microelectronics technology is not expected to reach similar levels because of its physical limitations (Fig. 2).

By imitating nature, scientists have already developed a growing array of electronic sensors and computing systems. It is obvious that we must continue to take cues from the world around us to identify the proper methods to enhance human knowledge and capability. However, future advances in this direction will have to reach closer to the structure of atoms, by engineering *nanoscale electronics* (Fig. 3).

Thanks to nanoelectronics, it will not be unforeseeable in the near future to *create* artificial atoms, molecules, and integrated multifunctional nanoscale systems. For example, as illustrated in Fig. 4, the structure of an atom can be likened to that of a so-called quantum dot or Q-dot where the three-dimensional potential well of the quantum dot replaces the nucleus of an atom. An artificial molecule can then be made from artificial atoms. Such artificial molecules will have the potential to revolutionize the performance of optoelectronics and electronics by achieving, for example, orders of magnitude higher speed processors and denser memories. With these artificial atoms/molecules as building blocks, artificial active structures such as nanosensors, nanomachines, and smart materials will be made possible.

At the foundation of this endeavor is solid state engineering, which is a fundamental discipline that encompasses physics, chemistry, electrical engineering, materials science, and mechanical engineering. Because it provides the means to understand matter and to design and control its properties, solid state engineering is key to comprehend Natural Science (Fig. 5).
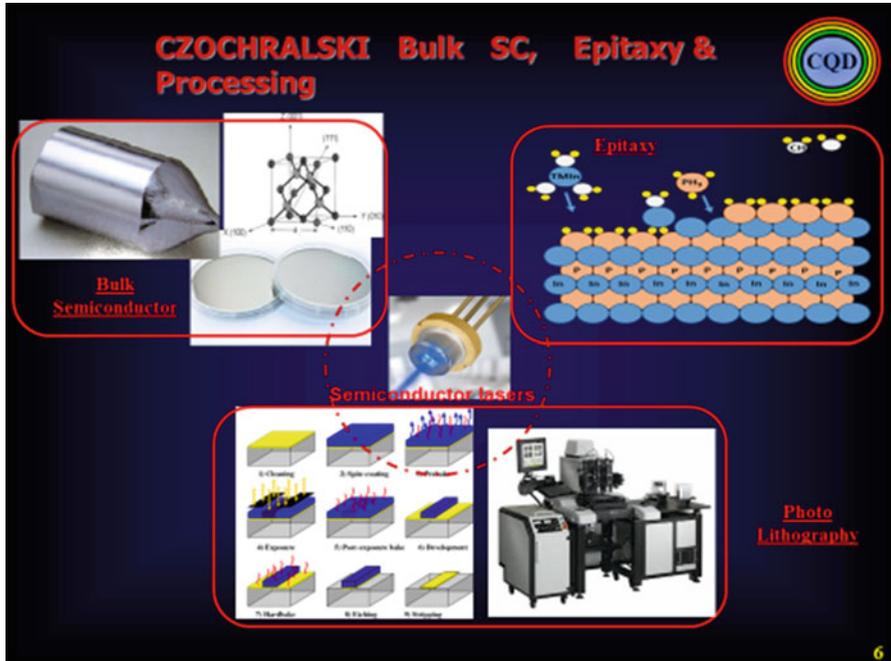
Fig. 3 The various ways a semiconductor is made as bulk (top left), with atomic beam deposition, and the way it is patterned and processed for device application using photolithography with laser beams to delimit regions
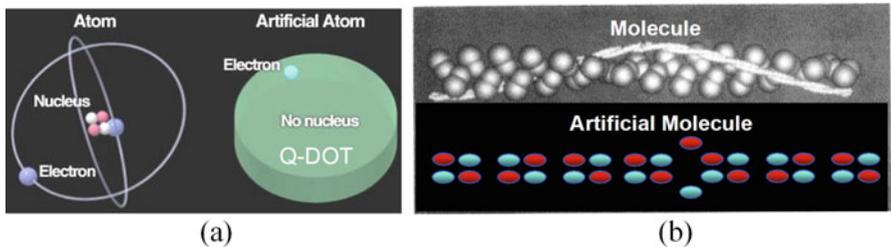
Fig. 4 Schematic comparisons: (**a**) between a real atom and an artificial atom in the form of a quantum dot and (**b**) between a real molecule and an artificial molecule

The twentieth century has witnessed the phenomenal rise of Natural Science and Technology into all aspects of human life. Three major sciences have emerged and marked that century, as shown in Fig. 3: Physical Science which has strived to understand the structure of atoms through quantum mechanics, Life Science which has attempted to understand the structure of cells and the mechanisms of life through biology and genetics, and Information Science which has symbiotically developed the communicative and computational means to advance Natural Science.
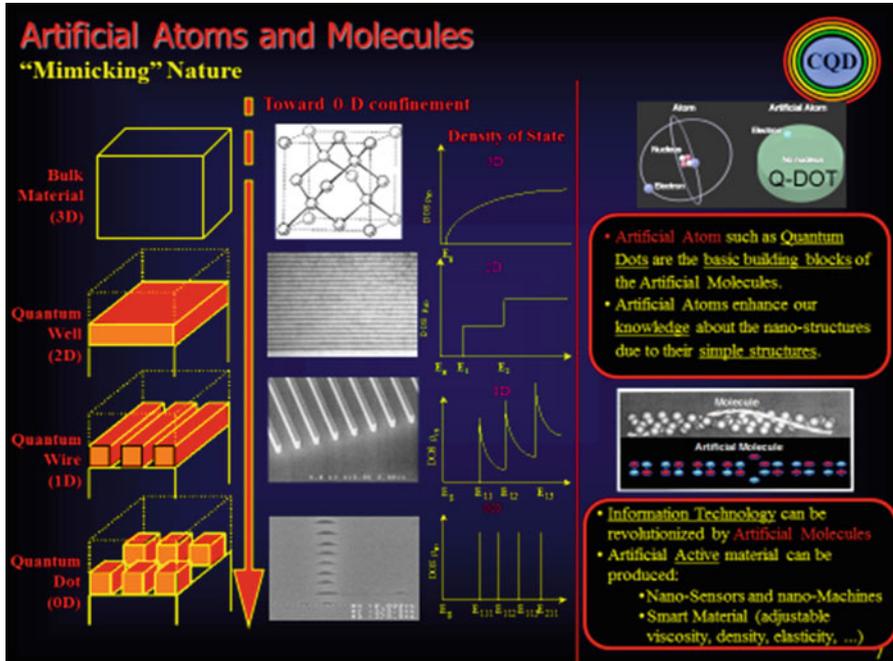
Fig. 5 The electronic structure and thus properties of materials, such as the density of available energy levels D(E), for example, changes with confinement size and dimensionality, and can be controlled by the great progress made using atom-by-atom deposition technologies such as MBE and MOCVD (molecular beam epitaxy and metalorganic chemical vapor deposition) areas in which the present author is a world leader

The scientific and technological accomplishments of earlier centuries represent the first stage in the development of Natural Science and Technology, that of understanding (Figs. 6 and 7). As the twenty-first century rolls in, we are entering the creation stage where promising opportunities lie ahead for creative minds to enhance the quality of human life through the advancement of science and technology.

Hopefully, by giving a rapid insight into the past and opening the doors to the future of solid state engineering, this course will be able to provide some of the basis necessary for this endeavor, inspire the creativity of the reader, and lead them to further explorative study.

Since 1992 when I joined Northwestern University as a faculty member and started to teach, I have established the Solid State Engineering (SSE) research group in the Electrical Engineering and Computer Science Department and subsequently created a series of related undergraduate and graduate courses. In the creative process for these courses, I studied similar programs in many other institutions such as Stanford University, the Massachusetts Institute of Technology, the University of Illinois at Urbana-Champaign, the California Institute of Technology, and the
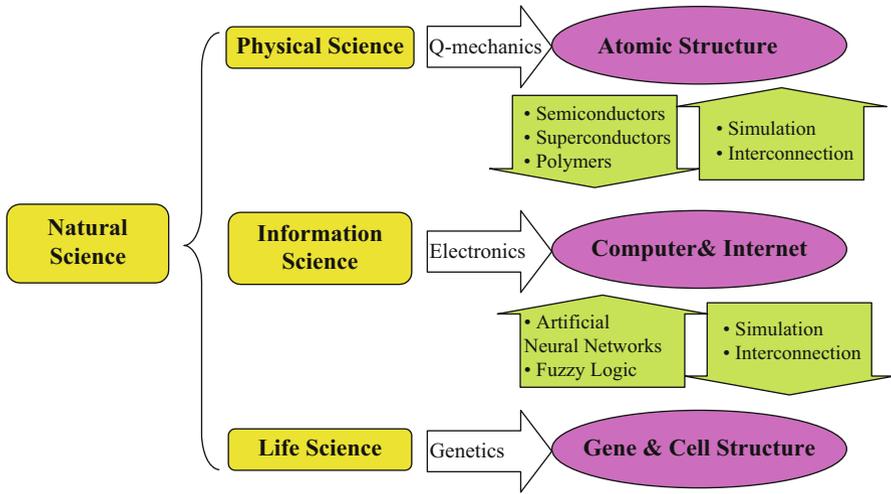
Fig. 6 Three branches of Natural Science and Technology have impacted all aspects of human life in the twentieth century: Physical, Information, and Life Sciences (▢). For each one, a key scientific discipline or technology has been developed: quantum mechanics, electronics, and genetics (⟹). These have allowed to both better understand the building blocks of nature (structures of atoms, genes, and cells) and develop the tools without which these scientific advances would not have been possible (computer and Internet) (⬭) in a synergetic manner (▱ ▱)
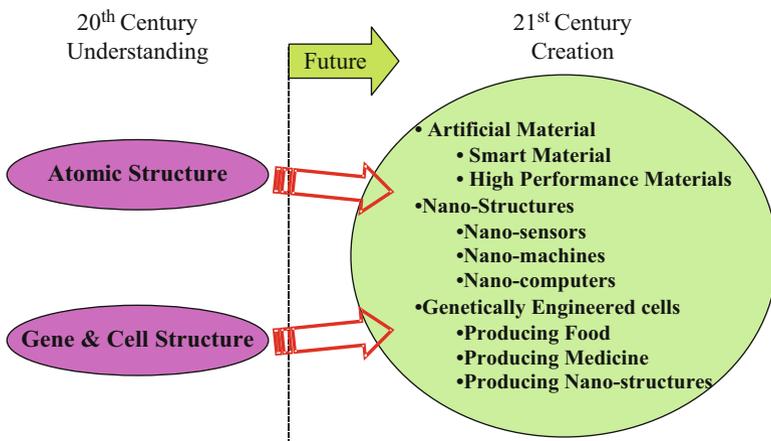
Fig. 7 The scientific and technological advances of the twentieth century can be regarded as the understanding stage in the development of Natural Science and Technology. The twenty-first century will be the creation stage in which novel opportunities will be discovered and carried out
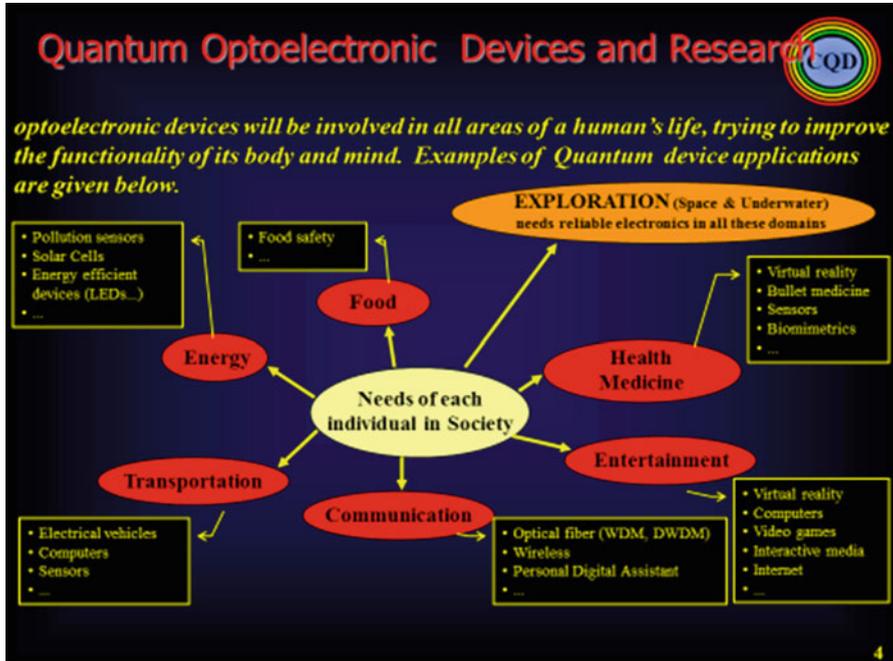
Fig. 8 The slide is self-explanatory: the many areas of life where solid state engineering has a direct impact

University of Michigan. I reviewed numerous textbooks and reference texts in order to put together the teaching material students needed to learn nanotechnology and semiconductor science and technology from the basics up to modern applications. But I soon found it difficult to find a textbook which combined all the necessary material in the same volume, and this prompted me to write the first edition of a textbook on the *Fundamentals of Solid State Engineering* (Fig. 8).

The book was primarily aimed at the undergraduate level, but graduate students and researchers in the field will also find useful material in it. After studying it, a student will be well versed in a variety of fundamental scientific concepts essential to solid state engineering, in addition to the latest technological advances and modern applications in this area, and will be well prepared to meet more advanced courses in this field.

In this fourth edition, I have taken into account the feedback and comments from students who took the courses associated with this text and from numerous colleagues in the field. The fourth edition is an updated, more complete text that covers an increased number of solid state engineering concepts and goes in depth in several of them. The chapters also include redesigned and larger problem sets.

This fourth edition is structured in two volumes. The first focuses on the basic physics concepts which are at the heart of solid state matter in general and semiconductors in particular. The text starts by providing an understanding of the

structure of atoms and electrons and the structure of matter (Chap. 1); a new chapter is devoted to the element carbon and its allotropes such as graphene, carbon nanotubes, and fullerenes (Chap. 2) and then the real and reciprocal crystal lattices (Chap. 3). An introduction to the basic concepts in quantum mechanics (Chap. 4) and to the modeling of electrons and energy band structures in crystals is then given in Chap. 5. Chapter 4 was extended in the fourth edition to include the Heisenberg equation of motion, the hydrogen atom, and the harmonic oscillator and quite a bit more. The new material now gives the student a reasonably complete description of the quantum mechanics tools that he needs. In Chap. 6 the attention is focused on the thermal and vibrational properties of crystals. The reader is introduced to the concept of phonons to describe vibrations of atoms in crystals (Chap. 6), and then later in the same chapter, he learns how to calculate the thermal properties of crystals. The equilibrium and non-equilibrium electrical properties of semiconductors are reviewed in Chaps. 7 and 8. First the statistics (Chap. 7) and then, later in Chap. 8, the transport description are developed. This now includes the Boltzmann equation approach. The problem of the generation and recombination properties of charge carriers in semiconductors is also considered in detail in Chap. 8. With these concepts one can now proceed to model semiconductor *p-n* and semiconductor-metal junctions (Chap. 9) which constitute the building blocks of modern electronics. The optical properties of semiconductors are described in Chap. 10. Solar, thermal, and photothermal harvesting of energy have been added in this new edition as Chaps. 11, 12, and 13. Screening and electron-electron interactions, on an elementary level, are the subjects of the new Chap. 14. This is followed by a discussion of semiconductor heterostructures and low-dimensional quantum structures including quantum wells and superlattices, wires, and dots in Chap. 15. The new Chap. 16 contains an introduction to the physics of quantum transport. A brief description of the coupling between electrons and lattice vibrations (electron-phonon interactions) then follows in the second part of Chap. 16. In the new and old chapters, the derivation of the mathematical relations has been spelled out in some detail, so that the reader can understand the limits of applicability of these expressions and adapt them to his or her particular needs. The final three chapters of the book focus on the growth and characterization of real semiconductor crystals. Chapter 17 introduces modern epitaxial and bulk semiconductor crystal growth techniques. This is followed by a discussion of semiconductor characterization techniques and defects in Chaps. 18 and 19.

In each chapter, a section "References" lists the bibliographic sources which have been referenced in the text. The interested reader is encouraged to read them in addition to those given in the section "Further reading."

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Contents

List of Symbols

a_0	Bohr radius
Å	Angstrom
α	Absorption coefficient
α_L	Thermal expansion coefficient
$\vec{B}$	Magnetic induction or magnetic flux density
c	Velocity of light in a vacuum
cal	Calorie
C, C_v, C_p	Heat capacity or specific heat, at constant volume, at constant pressure
d	Density
d	Distance, thickness or diameter
D, $\vec{D}$	Electric displacement
D, D_n, D_p	Diffusion coefficient or diffusivity, for electrons, for holes
Δn, Δp	Excess electron, hole concentration
$\vec{E}$	Electric field strength
E, E_n	Energy
E_C	Energy at the bottom of the conduction band
E_F	Fermi energy
E_{Fn}	Quasi-Fermi energy for electrons
E_{Fp}	Quasi-Fermi energy for holes
E_g	Bandgap energy
E_V	Energy at the top of the valence band
E_Y	Young's modulus
ε_0	Permittivity in vacuum
ε	Permittivity
ε_r	Dielectric constant
F, $\vec{F}$	Force
f	Frequency
f_e	Fermi-Dirac distribution for electrons
f_h	Fermi-Dirac distribution for holes
Φ_{ph}	Photon flux

Φ_B	Schottky potential barrier height
Φ_m, Φ_s	Work function of a metal, semiconductor
g	Gravitational constant
g	Density of states
G	Gibbs free energy
G, g	Gain
Γ	Optical confinement factor
H	Enthalpy
$\vec{H}$	Magnetic field strength
h	Planck's constant
$\hbar$	Reduced Planck's constant, pronounced "h bar", ($=h/2\pi$)
η	Quantum efficiency
η	Viscosity
i	$\sqrt{-1}$
i, I	Current
$J, \vec{J}$	Current density, current density vector
$J^{\mathrm{diff}}, \vec{J}^{\mathrm{diff}}$	Diffusion current density
$J^{\mathrm{drift}}, \vec{J}^{\mathrm{drift}}$	Drift current density
J_T	Thermal current
κ	Thermal conductivity coefficient
κ	Damping factor (imaginary part of the complex refractive index $\bar{N}$)
$\vec{K}$	Reciprocal lattice vector
$k, \vec{k}$	Wavenumber ($=2\pi/\lambda = 2\pi\nu/c$), wavenumber vector or wavevector
k_b	Boltzmann constant
k_D	Debye wavenumber
L_n, L_p	Diffusion length for electrons, holes
λ	Wavelength
Λ	Mean free path of a particle
m, M	Mass of a particle
m_0	Electron rest mass
m^*, m_e	Electron effective mass
m_h, m_{hh}, m_{lh}	Effective mass of holes, of heavy holes, of light holes
m_r^*	Reduced effective mass
M_V	Solid density (ratio of mass to volume)
μ	Permeability
μ_e	Electron mobility
μ_h	Hole mobility
n	Particle concentration
n	Electron concentration or electron density in the conduction band
n	Ideality factor in semiconductor junctions
$\bar{n}$	Refractive index (real part of the complex refractive index $\bar{N}$)

$\bar{N}$	Complex refractive index
N_A	Acceptor concentration
N_c	Effective conduction band density of states
N_D	Donor concentration
N_v	Effective valence band density of states
υ	Frequency
N_A	Avogadro number
p	Hole concentration or hole density in the valence band
$p, \vec{p}$	Momentum
P	Power
Ψ	Wavefunction
q	Elementary charge
Q	Total electrical charge or total electrical charge concentration
ρ	Electrical resistivity
$\vec{r}$	Position vector
$\vec{R}$	Direct lattice vector
R	Resistance
R	Reflectivity
Ra	Rayleigh number
Re	Reynolds number
R_0	Differential resistance at $V = 0$ bias
R_i	Current responsivity
R_v	Voltage responsivity
Ry	Rydberg constant
S	Entropy
σ	Electrical conductivity
τ	Carrier lifetime
U	Potential energy
V	Voltage
$v, \vec{v}$	Particle velocity
v_g	Group velocity
ω	Angular frequency ($= 2\pi\upsilon$)
$\vec{x}, \vec{y}, \vec{z}$	Unit vectors (Cartesian coordinates)