## CHAPTER I
INTRODUCTION TO SEMICONDUCTOR NANOMATERIALS

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1.1 Introduction to nanoscience and nanotechnology

Nanoscience and nanotechnology are the “Research and technology development at the atomic, molecular and macromolecular levels in the length scale of approximately 1-100 nanometer range, to provide a fundamental understanding of phenomena and materials at the nanoscale and to create and use structures, devices and systems that have novel properties and functions because of their small and/or intermediate size”.

As early as 1959, renowned physicist Richard Feynman suggested in his famous speech: “there’s plenty of room at the bottom” that it should be possible to build devices with atomic precision. “At the atomic level, their exist new kinds of forces, new kinds of possibilities and new kinds of effects. The problems of manufacture and reproduction of materials will be quite different”. In 1974, the term “nanotechnology” was formally introduced by Norio Taniguchi to describe a tiny world in which things would be measured in nanometers (nm). Since then, nanotechnology has progressed to the point where its use is common; if not fully mature [1].

Many physical phenomena in both organic and inorganic materials have natural length scales between 1 and 100 nm ($10^2$ to $10^7$ atoms). As an example, the average width of a human hair is of the order of $10^5$ nm, whereas, a single red blood cell is ~ 5,000 nm and a DNA molecule has a diameter of 2–12 nm. Nanotechnology is a synergism of concepts drawn from different branches of science and technology having the nanometer size as the most important characteristics in common. Started as a pure scientific interest a few years ago; the nanoparticles are nowadays considered as the stepping stones for the development of new cutting-
edge applications in communications, data storage, optics, energy storage and transmission, environmental protection, biology and medicine due to their relevant optical, electrical and magnetic properties. Their novel properties, not encountered in the case of their bulk counterparts, can lead to a potentially tremendous scientific and technological progress. Moreover, all these potential applications are expected to impact profoundly every aspect of modern living.

Unlike their bulk counterparts, nanomaterials present a reduced dimensionality associated with a very high surface to volume ratio that increases with decreasing particle size. Consequently, a larger fraction of the constituting atoms will be found at the surface of the particles, rendering them highly reactive and inducing specific properties [2]. Since the intrinsic properties of the nanoparticles, such as composition, crystallinity, size and surface topography are crucial for their physical properties, the control of the structural characteristics through the chemical synthesis is highly desired. Controlled physical size of the materials can be used to tune their properties. For example, the electronic and optical properties of metals and semiconductors strongly depend on the crystallite size in the nanometer size regime [3,4]. Uncovering and mapping materials with size dependent properties require synthetic routes to prepare homologous size series of monodisperse nanometer size crystals, known as nanocrystals.

1.2 Fundamentals of semiconductor

Semiconductors are a group of materials having electrical conductivities intermediate between metals and insulators. It is significant that the conductivity of these materials can be varied over orders of magnitude by changes in temperature, optical excitation and impurity
content. It is very small in size and sensitive to heat, light and electricity. It is very useful in cell phones, home appliances and medical equipments. If impurities are added to a semiconductor its electrical conductivity increases. Similarly, if the temperature of a semiconductor is increased its electrical conductivity increases.

Semiconductor - based electronic components comprise transistors, solar cells, many kinds of diodes including the light emitting diode, the silicon controlled rectifier, photo-diodes, and digital and analog integrated circuits. Increasing understanding of semiconductor materials and fabrication processes has made possible continuing increases in the complexity and the speed of semiconductor devices, an effect is known as Moore’s Law [5].

Germanium and silicon are distinctive elemental semiconductors, III-V and II-VI compounds, such as gallium arsenide and zinc oxide are compound semiconductors. Basically the semiconductors are classified into two types, namely intrinsic semiconductor or pure semiconductor and extrinsic semiconductor or doped semiconductor.

Furthermore, the conductivity can be changed by irradiation with light or high energy electrons or by the injected carriers. In such a semiconductor, charge transport may be either by electrons or holes, depending on the type of doping. The periodicity of a semiconductor lattice introduces the concepts of the reciprocal lattice and the Brillouin zone, resulting to specify the energy levels in a semiconductor in terms of energy with momentum. All semiconductors can be classified either as direct gap semiconductors with a valence band maximum or a conduction band minimum occurring at the same point in the Brillouin zone, or as
indirect gap semiconductors in which these extreme occur at different points in the Brillouin zone. The optical properties of direct gap semiconductors differ considerably from those of indirect gap semiconductors [6, 7].

1.3 Semiconductor nanoparticles

The properties of crystalline solids are not noticed by their size in general. It is only in the regime below 10 nm in which this variable comes into play. In the past decades, tailoring of material characteristics by size control has been demonstrated in many inorganic solids, especially on the technological point of view. For an example, the bandgap can be tuned between 2.5 and 4 eV for CdS. Similarly in CdS nanoparticles, the melting temperature varies from 1600°C down to 400°C by varying its size [8]. Also, the pressure required to induce transformation from a four to a six-coordinate phase increases from 2 to 9 GPa, even as the number of nucleation events for the transition becomes same [9]. Thus, it is demonstrated that enormous range of fundamental properties is all realized in CdS prepared in nanoform and the same can be extended to other materials by controlling their size. The variation is achieved by reducing the size of the crystal and not by altering its chemical composition.

There are two major effects which are responsible for these size variations in nanocrystal properties. First, in nanocrystals, the number of surface atoms is in large fraction of the total volume. Second, the intrinsic properties of the interior of nanocrystals are transformed by quantum size effects. In any material, surface atoms make a distinct contribution to the free energy and the large changes in thermodynamic properties of
nanocrystals such as melting temperature depression and solid-solid phase transition elevation can ultimately be traced.

More recent work shows that nanocrystals assume regular shapes with the same well defined facets as present in extended crystals. This opens up the possibility of manipulating the surface energetics of nanocrystals in a controlled manner. The ability to manipulate the energetics of nanocrystal surfaces would have practical consequences. Nanocrystals are observed to occur in the same crystal structure as the extended solid [10]. To prepare nanocrystals with interior bonding geometries that do not occur in the known extended solid, by appropriately adjusting the surface energy. Thus, nanocrystals with entirely distinct properties from their extended counterparts may be envisioned [11].

Independent of the large number of surface atoms, semiconductor nanocrystals with the same interior bonding geometry as a known bulk phase often exhibit strong variations in their optical and electrical properties with size [12]. These changes arise through systematic transformations in the density of electronic energy levels as a function of size of the interior known as quantum size effects.

As a function of increasing size, the center of a band develops first and the edges develop last. Thus, in metals, where the Fermi level lies in the center of a band, the relevant energy level spacing is still very small and at temperatures above a few Kelvin, the electrical and optical properties more closely resemble those of a continuum [13]. However, in semiconductors, the Fermi level lies between two bands, so that the edges of the bands dominate the low-energy optical and electrical behavior.
Optical excitations across the gap depend strongly on the size, even for crystallites as large as 10,000 atoms. The electrical transport properties of nanocrystals also depend strongly on size. The energy required to add successive charges into an extended crystal does not vary. In a nanocrystal, the presence of one charge acts to prevent the addition of another. Thus, in metals or semiconductors, the current-voltage curves of individual crystallites resemble a staircase, due to Coulomb blockade [14]. The electrical characteristics of individual semiconductor nanocrystals, in which Coulomb blockade effects and discrete energy level spacings are both expected to occur, are a topic of interesting research [15].

Despite the seeming perfection of a pure cluster in the gas phase, from the point of view of semiconductor physics, it is a highly defective system in many ways. At the surface of a pure semiconductor, substantial reconstructions in the atomic positions occur and thereby invariably energy levels lie within the energetically forbidden gap of the bulk solid. These surface states act as traps for electrons or holes and degrade the electrical and optical properties of the material. Passivation is the chemical process by which these surface atoms are bonded to another material having much larger bandgap in such a way that to eliminate all the surface traps inside the gap. The ideal termination naturally removes the structural reconstructions, leaving no strain and simply produces an atomically abrupt jump in the chemical potential for electrons or holes at the interface. The termination of Si with SiO₂ and that of Al₁₋ₓGaₓAs with GaAs are probably the best known examples of successful passivation. One of the most powerful features of these methods is that the low-dimensional semiconductor structure is completely embedded inside
another material with larger bandgap providing a high degree of surface passivation.

Over decades, the ability to control the surface of semiconductors with near atomic precision has led to a further idealization of semiconductor structures such as quantum wells, wires and dots. It is possible to imagine simple geometric objects of differing dimensionality (2D, 1D and 0D), each case made out of homogeneous semiconductor material with perfect surface termination. Such structures should exhibit the idealized variations in density of electronic states predicted by a simple particle in a box type model of elementary quantum mechanics with the continuous levels of the 3D evolving into the discrete states of zero dimensional structures.

From the perspective of solid state physics and materials science, it is perhaps surprising that nanocrystals of inorganic solids, coated with organic ligands, have been proved as one of the most diverse and powerful ideals of a quantum dot. This is because, the nanocrystal can now be considered not just a component embedded in the surface of a solid state device, but rather a chemical reagent. In this form, the nanocrystal may be dissolved in a fluid, spun into a polymer, attached to an electrical circuit, bound to other nanocrystals as dimers, trimers etc., or perhaps bound to biological molecules. It is important to realize that in the construction of optical and electronic materials using components of nanometer size, it is not only the physical properties of matter that changes, but also the chemical methods by which the materials are constructed. This is clearly demonstrated in case of SiO$_2$ coated Si nanocrystals [16,17] and in oxidized InP nanocrystals [18]. It is also seen that nanocrystals are grown inside glass. Indeed, there are even analogs to
quantum wells in which the layers of inorganic solids are grown in successive shells around one another epitaxially. The best documented example is the CdS/HgS/CdS quantum dot quantum well [19,20]. In each case, the final product is still small enough that a final layer of ligands bound to the outer surface is sufficient to confer solubility and open the use of these solid state materials to the world of chemical synthesis.

Nanomaterials can be classified into nanostructure materials and nanoparticulate materials; the former group is about condensed bulk materials that contain grains or composites with sizes that are in the nanometer range, the later are dispersed or colloidal nanoparticles (NPs). Nanotechnology is expected to create new materials with totally new problem-solving properties. The Nanoparticles are applicable in a variety of fields like miniaturized devices, light-emitting diodes, photovoltaic, lasers and optical memory or as fluorescent probes for diagnostic markers in biology [21-23]. Nanoparticles can be considered as a single crystal of a typical size of a few nanometers consisting of 100’s to 1,000,000’s of atoms, which preserve some of the attributes of the bulk material but exhibit in addition very interesting properties due to the size quantization effect. The NPs can be in a variety of state from pure or mixed solid materials to the state of powder, thin films or colloidal solutions. The name quantum dot is also often used for highly fluorescent nanocrystals and newly commercially available fluorescent nanoparticles.

The following list enumerates some examples of materials which can be produced in the nanometer range giving rise to nanoparticles [19,24, 25]:

11
1. Metals: gold, silver, palladium, platinum, cobalt,
2. Oxides: ZnO, TiO$_2$, SnO$_2$ and
3. Semiconductors: silicon, II-VI (CdS, CdSe, CdTe, ZnS, ZnSe), III-V (GaAs, GaP, GaN, InAs, InP) and the IV-VI group (PbS, PbSe, PbTe).

### 1.4 Classification of semiconductors

#### 1.4.1 Elemental semiconductors

Basically, semiconductors are classified into elemental and compound semiconductors. Elemental semiconductors are made from a single element of IV group elements of the periodic table. It is also known as indirect bandgap semiconductors. These are most often made up of germanium (Ge) and silicon (Si). In addition, germanium is the prototype of a large class of semiconductors with similar crystal structures. The crystal structures of Si and Ge are the same as that of diamond and $\alpha$-tin. In this structures, each atom is surrounded by four nearest neighbor atoms (each atom is said to be four-fold coordinated), forming a tetrahedron. These tetrahedrally bonded semiconductors form the mainstay of the electronics industry and the cornerstone of modern technology. Some elements from the groups V and VI of the periodical table, such as phosphorus (P), sulfur (S), selenium (Se) and tellurium (Te), are also semiconductors. The atoms in these crystals can be three-fold (P), two-fold (S, Se, Te) or four-fold coordinated. As a result, these elements can exist in several different crystal structures and they are also good glass-formers. For an example, Selenium (Se) has been grown with monoclinic and trigonal crystal structures or as a glass [26].
1.4.2 Compound semiconductors

Compound semiconductors are formed by combining III and V group elements or II and VI group elements in the periodic table. It is also known as direct bandgap semiconductors. These include indium and antimony, indium and arsenic, gallium and phosphorus, gallium and antimony, gallium and arsenic, silicon and carbon and gallium and nitrogen. Most of the II-VI compound semiconductors have bandgaps larger than 1eV, except mercury (Hg). Mercury telluride (HgTe) is actually a zero bandgap material. Large bandgap II-VI compounds semiconductors have potential applications for displays and lasers, the smaller bandgap II-VI semiconductors are important materials for the fabrication of infrared detectors. The I-VII compounds (e.g. CuCl) tend to have even larger bandgaps (>3 eV) as a result of their higher ionicity.

The large ionicity compounds are also favours six-fold coordinated ions. They are similar to the mercury chalcogenides and they have very small bandgaps in spite of their large iconicity. These small bandgap IV-VI semiconductors are also important as infrared detectors. GaN, a large bandgap III-V compound, and the mixed crystals gallium indium nitride (Ga_{1-x}In_{x}N) are being used for blue light emitting diodes and lasers [27,28].

1.4.3 Oxide semiconductors

The oxide semiconductors are not well understood with regard to their growth processes, so they have limited potential for applications at present. Some oxides such as cupric oxides and cuprous oxide are well known semiconductors. Likewise oxides are good insulators. Cuprous oxide occurs as a mineral (cuprite), it is a classic semiconductor. The
high-Tc superconductor, based on the semiconductor lanthanum copper oxide (La$_2$CuO$_4$) has a bandgap of about 2 eV.

### 1.4.4 Layered semiconductors

Some well known layered semiconductors are lead iodide (PbI$_2$), molybdenum disulfide (MoS$_2$) and gallium selenide (GaSe). These materials are characterized by their layered crystal structures. It is basically a covalent and much stronger than the Vander waal’s forces between the layers. These layered semiconductors are of interests, because the behavior of electrons in the layers is quasi-two-dimensional. The layered structure is made of a material called molybdenum disulfide which belongs to a new class of semiconductors; metal di-chalogenides replace today's technology, complementary metal oxide semiconductors, or CMOS.

### 1.4.5 Organic semiconductors

Organic compounds such as polyacetylene [(CH$_2$)$_n$] and polydiacetylene are semiconductors. The advantage of organic over inorganic semiconductors is that they can be easily tailored to the applications for device fabrication. Recently, organic semiconductors have been used to realize novel, self-emitting display based on organic light emitting diodes (OLED). Also, there are good prospects for further applications, such as organic solar cells and plastic electronics. The bandgaps of these compounds can be changed more easily than inorganic semiconductors by changing their chemical formulae. Recently new forms of carbon, such as C$_{60}$ (fullerene), have been found to be semiconductors. One form of carbon consists of sheets of graphite rolled into a tube of some nanometers in diameter known as nanotubes [29,30].
1.4.6 Magnetic Semiconductors

Magnetic semiconductors exhibit the dual properties of both ferromagnetic and semiconductor properties. Compounds containing magnetic ions such as europium and manganese have interesting semiconducting and magnetic properties. Examples of these magnetic semiconductors include EuS and alloys such as Cd$_{1-x}$Mn$_x$Te. Depending on the amount of the magnetic ion in these alloys, the latter compounds exhibit different magnetic properties such as ferromagnetism and antiferromagnetism. The magnetic alloy semiconductors containing low concentrations of magnetic ions are known as dilute magnetic semiconductors. These alloys have recently attracted much attention because of their potential applications. Faraday rotations can be up to six orders of magnitude larger than those of nonmagnetic semiconductors. As a result, these materials can be used as optical modulators based on their large magneto optical effects.

1.4.7 Narrow and wide bandgap semiconductors

Narrow gap semiconductors are members of the semiconductors family with narrow forbidden fundamental bands. It has forbidden band width $E_g$ smaller than 0.5eV and large dielectric constant. The characteristics of the energy bands of narrow gap materials include strongly non parabolic conduction bands. HgCdTe alloys and InSb are used as infrared detectors or thermoelectrics. The wide bandgap (WBG) semiconductor materials have energy bandgaps roughly 2-3 times that of silicon. The most important wide bandgap semiconductors are the group of materials called the III nitrides. The III nitrides are compound semiconductors formed by combining III group elements in the periodic table with nitrogen. The most important binary compounds are GaN, AlN and InN and ternary compounds are GaInN, AlGaN and InAlN. WBG
Semiconductors permit devices to operate at much higher temperatures, voltages and frequencies making the power electronic modules using these materials significantly more powerful and energy efficient than conventional semiconductor materials [31]. WBG materials also emit light in the visible color range, an optical property useful for applications in solid state lighting. Gallium nitride (GaN) is an enabling material behind the ultra-high efficiency of light emitting diodes (LEDs).

The strain induced polarization fields can alter the band bending and carrier concentration at the interface. The strain associated with the lattice mismatch of the GaN and AlGaN layers generates a piezo electric polarization that acts perpendicular to the heterointerface. The piezo electric polarization of the strained AlGaN layer is much greater than that of AlGaAs/GaAs structures by a factor of 5 [32]. Wide bandgap semiconductors offer numerous advantages over conventional silicon, gallium arsenide and indium phosphide electronics. Some attractive commercial applications of wide bandgap electronic devices include power amplifiers for base stations in wireless networks, automotive and aviation electronics, in which high temperature operation is needed and in high voltage switching for power systems and electric vehicles [33].

1.4.8 Direct and indirect bandgaps

Semiconductors are classified based on their bandgap values between conduction band and valance band into two different types namely direct and indirect bandgap semiconductors. For a direct bandgap material, the minimum of the conduction band and maximum of the valance band lies at the same momentum, \( k \) and values. When an electron presents at the bottom of the conduction band recombines with a hole at the top of the valance band, there will be no change in momentum values. Energy is conserved by means of emitting a photon, such transitions are
called as radiative transitions. Fig.1.1a shows energy with crystal momentum for a semiconductor with a direct bandgap. It shows that an electron can shift from the lowest energy state in the conduction band to the highest energy state in the valence band without a change in crystal momentum [34].

The minimum of the conduction band and maximum of the valance band lie at different k-values for an indirect bandgap material. When an electron and a hole recombine in an indirect-bandgap semiconductor, phonons must be involved to conserve momentum. Fig.1.1b shows the crystal momentum for a semiconductor with an indirect bandgap. An electron cannot shift from the lowest-energy state in the conduction band to the highest-energy state in the valence band without a change in momentum [35].

1.5 Properties of semiconductor

1.5.1 Variable conductivity

The conductivity of semiconductor is poor consequence of having just the right number of electrons to completely fill its valence bands. Through various techniques (e.g., doping or gating), the semiconductor can be modified to have excess of electrons or a deficiency of electrons. In both cases, the semiconductor becomes much more conductive (the conductivity can be increased by one million fold or more). This doping technique is exploited by semiconductor devices to shape electrical current.
Fig. 1.1a Direct bandgap semiconductor

Fig. 1.1b Indirect bandgap semiconductor
1.5.2 Depletion

When doped semiconductors are joined to metals, to different semiconductors and to the same semiconductor with different doping, the resulting junction often strips the electron excess or deficiency out from the semiconductor near the junction. This depletion region is rectifying (only allowing current to flow in one direction), and used to further shape electrical currents in semiconductor devices.

1.5.3 Energetic electrons travel far

Electrons can be excited across the energy bandgap of a semiconductor by various means. These electrons can carry their excess energy over the distance scales of microns before dissipating their energy into heat a significantly longer distance than is possible in metals. This property is essential for the function of diodes, bipolar junction transistors and solar cells.

1.5.4 Light emission

Some semiconductors are used in the construction of light emitting diodes and fluorescent quantum dots due to relaxation of electrons by emitting light in place of producing heat.

1.5.5 Thermal energy conversion

Semiconductors are useful in thermoelectric generators as they have large thermoelectric power factors like wise high thermoelectric figures of merit making them useful in thermoelectric coolers.

1.6 Low dimensional semiconductors

Semiconductor based light sources and detectors are critically important to this emerging technology. When one or more of the dimensions of a solid are reduced sufficiently, its physicochemical
characteristics notably depart from those of the bulk solid. With reduction in size, novel electrical, mechanical, chemical, magnetic and optical properties can be introduced. The resulting structure is then called a low-dimensional structure or system. The confinement of particles, usually electrons or holes, to a low dimensional structure leads to a dramatic change in their behaviour and to the manifestation of size effects that usually fall into the category of quantum-size effects. Progress in optoelectronics has occurred not so much by device scaling as by new device physics. A semiconductor hetero structure can have a quantum confinement in zero dimension (bulk structure), one dimension (quantum well), two dimensions (quantum wire), or three dimensions (quantum dot) [36]. The use of quantum wells in the active region of lasers has reduced threshold current density by an order of magnitude [37].

1.6.1 Bulk structure

Objects having an overall size in non-nanometric range (mainly in micrometer or millimeter range), but displaying nanometric features (such as nanosized confinement spaces) or resulting from the periodic arrangement and assembly of nanosized building blocks can be classified as 3D nanosystems. They exhibit properties which differ from both molecular and bulk properties and as they extend along all three dimensions as shown in below Fig.1.2, they cannot be listed among the above mentioned 0D, 1D or 2D nanosystems. In particular, 3D nanocrystals and 3D superstructures are prepared by assembling together basic nanosized building blocks, such as 0D spheres, 1D rods and 2D plates, in order to have structures with larger size and with innovative shapes. On contrary, nanoporous materials are made in a complementary approach since a system of nano sized void pores is obtained within a continuous bulk material.
Fig. 1.2 Bulk structure in three dimensions
Simpler nanosystems can otherwise be used as artificial atoms to build three-dimensional superstructures such as super lattices in which a given nanoparticle is in a predictable and periodic lattice point. For this purpose, 0D nanosystems (and mainly nanoparticles) are the best choice, since they can easily lead to highly ordered 3D close packed patterns kept together by chemical interparticle interactions.

1.6.1.1 Density of states in 3D

The density of states refers to a number of quantum states per unit energy. In other words, the density of states, denoted by \( g(E) \), indicates how densely packed quantum states in a particular system. \( g(E) \, dE \) is expressed as

\[
g(E)dE = \frac{a^3}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E} \, dE
\]

where \( a \) is the width of the barrier. \( g(E)dE \) represents the number of states between \( E \) and \( dE \). The wave function is valid at regular intervals of \( \frac{\pi}{a} \).

1.6.2 Quantum well

If one dimension is reduced to the nano range while the other two dimensions remain large. To create quantization is to confine particles which are originally free to move in three dimensions, to two dimensions, forcing them to occupy a planar region. The effects of quantum confinement take place when the quantum well thickness becomes comparable to the De Broglie wavelength of the carriers (generally electrons and holes), leading to energy levels called energy subbands. A quantum well is often realized with a thin layer of a semiconductor medium, embedded between other semiconductors layers of wider bandgap is shown in Fig.1.3.
Fig. 1.3 AlGaAs/GaAs/AlGaAs quantum well structure
The thickness of such a quantum well is typically ~5–20 nm. Such thin layers can be fabricated with molecular beam epitaxy (MBE) or metal–organic chemical vapour deposition (MOCVD). Both electrons and holes can be confined in semiconductor quantum wells. In optically pumped semiconductor lasers, most pump radiation may be absorbed in the layers around the quantum wells and the generated carriers are captured by the quantum wells.

1.6.2.1 Density of states in 2D

In 2D, an electron is confined along one dimension but able to travel freely in the other two directions. In the Fig.1.4, an electron would be confined in the z-direction but would travel freely in the XY plane. For example, instead of using the volume of a shell, the area of a ring with width of dk is used. Analogous to the sphere in three dimensions, the circle is used because all points on the circle are an equal distance from the origin; therefore, the circle indicates equal values of energy. The radius becomes \( k = \sqrt{k_x^2 + k_y^2} \). In the 2D case, the unit cell is simply a square with side length of \( \frac{\pi}{a} \)

\[
g(E) dE = \frac{a^2 m}{\pi \hbar^2} dE \quad (1.2)
\]

1.6.2.2 Fabrication of quantum well

Quantum well structures can be grown by molecular beam epitaxy or chemical vapour deposition with control of the layer thickness down to monolayers. Thin metal films can also support quantum well states, in particular, metallic thin over layers grown in metal and semiconductor surfaces. The electron (or hole) is confined by the metal interface in one side, in general, by an absolute gap with semiconductor substrates, or by a projected bandgap with metal substrates.
Fig. 1.4 Density of states in 2D
1.6.2.3 Applications of quantum well

Quantum wells are formed in semiconductors by having a material, like gallium arsenide sandwiched between two layers of a material with a wider bandgap, like aluminium arsenide. Small red laser diodes are used as laser pointers.

Low power laser diodes are used in scanners, bar code reader laser printers and high electron mobility transistors. Quantum well infrared photo detectors are also based on quantum wells and are used for infrared imaging.

Broad area laser diodes, diode bars and diode stacks are often used for diode pumping of solid state lasers. Fiber coupled broad area laser diodes serve as pump sources of fiber amplifiers. Quantum well can be fabricated as saturable absorber utilizing its saturable absorption property. Saturable absorber is widely used in passively mode locking lasers. A major advantage of semiconductor saturable absorber mirrors have over other saturable absorber techniques is that absorber parameters can be easily controlled over a wide range of values. Fibre lasers working at $\sim 1 \mu m$ and $1.5 \mu m$ were successfully demonstrated earlier [38].

1.6.3 Quantum wire

If two dimensions are reduced to the nanorange and one remains large, the resulting structure is called as a quantum wire. In condensed matter physics, a quantum wire is an electrically conducting wires in which quantum effects influence the transport properties. A typical example of an n-type GaAs/AlGaAs quantum wire shown in Fig.1.5 in which the electrons in the GaAs layer are confined in both the growth direction $z$ direction and $y$ direction, but they can move along the $x$ direction.
Fig.1.5 AlGaAs/GaAs/AlGaAs quantum wire structure
1.6.3.1 Density of states in 1D

The density of states for a 1D quantum mechanical system exhibits a unique solution which has application in things such as nanowires and carbon nanotubes. In both x and y directions, the electron is confined, but it moves freely in the z direction changing from 2D to 1D.

The unit cell becomes a line segment of length $\frac{\pi}{a}$. Just as a ring is used in the 2D system to find the number of quantum states in a differential interval of energy, so a line segment is used in the 1D situation. The line segment stretches from k to $k + dk$ or E to $E + dE$ and the length of the line is simply $dE$.

$$g(E)dE = \left[ \frac{a}{\pi} \sqrt{\frac{2m}{\hbar^2}} \frac{1}{\sqrt{E}} \right] dE$$ (1.3)

1.6.3.2 Fabrication of quantum wire

A standard quantum well layer can be patterned with photolithography or perhaps electron-beam lithography and etched to leave a free standing strip of quantum well material the latter may or may not be filled in with an overgrowth of the barrier material. Any charge carriers are still confined along the heterostructure growth (z) axis, as they are in the quantum well, but in addition (provided the strip is narrow enough) they are now confined along an additional direction, either the x - or the y-axis, depending on the lithography [39]. The following Fig.1.6 shows an expanded view of a single quantum wire where clearly the electron (or hole) is free to move in only one direction, in this case along the y-axis.
Fig. 1.6 Fabrication of quantum wire

Ga$_{1-x}$Al$_x$As

GaAs
The carbon nanotube is an example of a quantum wire. A metallic single-walled carbon nanotube that is sufficiently short to exhibit no internal scattering (ballistic transport) has a conductance that approaches two times the conductance quantum, $4e^2/h$. The factor of two arises because carbon nanotubes have two spatial channels [40].

1.6.3.3 Applications of quantum wire

A quantum wire application is nanobarcodes which is used in medical field [41]. However, they may complement or replace carbon nanotubes in some applications. After p-n junctions were built with quantum wires, the next logical step was to build logic gates. By connecting several p-n junctions together, researchers are able to create the basis of all logic circuits such as the AND, OR, and NOT gates are built from semiconductor quantum wire crossings. Semiconductor quantum wire crossings are considered to be important for the future of digital computing [42]. Conducting quantum wires offer the possibility of connecting molecular-scale entities in a molecular computer. Quantum wires appear in bundles, they may be used as tribological additives to improve friction characteristics and reliability of electronic transducers and actuators.

1.6.4 Quantum dot

Quantum dots were discovered in the early 1980s by Alexei Ekimov in a glass matrix and by Louis E. Brus in colloidal solutions [43]. The term quantum dot was coined by Mark Reed [44].
A quantum dot is a portion of matter whose excitons are confined in all three spatial dimensions. It is a nanocrystal made of semiconductor materials that are small enough to display quantum mechanical properties, specifically its excitons are confined in all the three spatial dimensions. The electronic properties of these materials are intermediate between those of bulk semiconductors and of discrete molecules [45,46].

Quantum dots are investigated as agents for medical imaging and hope to use them as qubits. Quantum of the same material, but with different sizes, can emit light of different colours. The physical reason is the quantum confinement effect. The larger dot, the redder its fluorescence spectrum. Conversely, smaller dots emit bluer light as shown in Fig.1.7. The coloration is directly related to the energy levels of the quantum dot.

Generally, the smaller the size of the crystal, the larger the bandgap, the greater the difference in energy between the highest valence band and the lowest conduction band becomes, therefore more energy is needed to excite the dot and concurrently, more energy is released when the crystal returns to its resting state. Quantum dots of different sizes can be assembled into a gradient multi-layer nanofilm. Quantum dot containing electrons can also be compared to atoms both have a discrete energy spectrum and bind a small number of electrons.
Fig. 1.7  Quantum dots sorted by size emitting light of different colours
1.6.4.1 Density of states in 0D

When considering the density of states for a 0D structure (i.e. quantum dot), no free motion is possible. Because there is no k-space to be filled with electrons and all available states exist only at discrete energies as shown in Fig.1.8, the density of states for 0D with the delta function is defined as

\[ g(E)_{0D} = 2 \delta (E-E_c) \]  \hspace{1cm} (1.4)

1.6.4.2 Applications of quantum dots

Quantum dots are useful for a variety of applications in transistors, solar cells, LEDs and diode lasers. They have also investigated quantum dots as agents for medical imaging and as possible qubits in quantum computing. Quantum dot technology is one of the most promising candidates for use in solid-state computation.

The perhaps oldest application of quantum dots is the formation of beautiful colors in stained glasses, e.g. in church windows. Quantum dots make possible fabrication of laser diodes with very low threshold pump power and low temperature sensitivity. Quantum dots can be used in white light-emitting diodes (LEDs): they are excited with a blue or near-ultraviolet LED and emit red and green light (acting as a kind of phosphor), so that overall a white color tone is achieved as shown in Fig.1.9. In semiconductor saturable absorber mirrors, quantum dots can serve as absorbers with a very low saturation fluence (typically 1 to 100mJ / cm²) [47].
Fig.1.8 Density of states in quantum dot

Fig.1.9 Quantum dot LEDs
Such quantum dot absorbers can also be contained in a glass matrix. Quantum dots can be parts of very sensitive photo detectors and in the future they may function in efficient photovoltaic cells. In the context of quantum cryptography, quantum dots can serve as single-photon emitters. Quantum dots might also be suitable for performing quantum computations. The mentioned functions can also be realized in the context of quantum nanophotonics. Quantum dot flour dyes have 15-20nm fluorescence lifetime which will enable them to study the signal noise ratio effectively [48].

1.6.5 Core-shell nanostructures

Surface engineering is an important tool to control the properties of the nanocrystals (NCs) and in particular the optical materials. One important strategy is the over growth of NCs with a shell of a second semiconductor resulting in core-shell (CS) system. This method has been successfully applied to improve the fluorescence quantum yield and the stability against photo-oxidation by proper choice of the core and shell materials to tune the emission wavelength in a large spectral window. After pioneering work in 1980’s and the development of powerful chemical synthesis routes at the end of 1990’s [49-51]. Nowadays, almost any type of core NCs prepared by a robust chemical synthesis method has been over grown with shells of other semiconductor materials. Depending on the bandgap and the relative position of electronic energy levels of the involved semiconductors, the shell can have different functions in core-shell nanocrystals (CSNCs).

1.6.5.1 Types of core-shell nanocrystals

Two main cases can be distinguished as type I and type II band alignment respectively. In the former, the bandgap of the shell material is larger than that of the core one and both electrons and holes are confined
in the core. In the latter, either the valence band edge or the conduction band edge of the shell material is located in the bandgap of the core. The resulting staggered band alignment leads upon excitation of the NC to a special separation of the hole and the electron in the different regions of the CS structure. Type I hetero structures experience optical transition between electron and hole states whose wave functions are localized in the same region in the real space whereas for type II hetero structures, the electron and hole lie in different regions (here, the core and shell of the NCs).

In type I CSNCs, the shell is used to passivate the surface of the core with the goal to improve its optical properties. The shell separates physically the surface of the optically active core NC from its surrounding medium. As a consequence, the sensitivity of the optical properties in the local environment of the NCs surface, induced by the presence of oxygen or water molecules, is reduced. With respect to core NCs, CS systems generally enhance the stability against photo degradation. At the same time, shell growth reduces the number of surface dangling bonds, which can act as trap states for charge carriers and reduce the fluorescence quantum yield (QY). The first published prototype system was CdSe/ZnS \[49\] where the ZnS shell significantly increases the fluorescence QY and stability against photo bleaching as shown in Fig 1.10. Shell growth is accompanied by a small shift (5-10 nm) of the excitonic peak in the UV-vis absorption spectrum and the PL wavelength. This observation is attributed to a partial leakage of the exciton in to the shell material.
Fig.1.10 CdSe/ZnS core-shell nano structure
In type II systems, shell growth aims at a significant red shift of the emission wavelength of the NCs. The staggered band alignment leads to a smaller effective bandgap than each one of the constituting core and shell materials. The interest of these systems is to tune the emission colour with the shell thickness towards spectral ranges which are difficult with other materials. Type II CSNCs have been developed in particular for near IR emission using CdTe/CdSe or CdSe/ZnTe. The PL decay times are strongly prolonged in type II CSNCs due to the lower overlap of the electron and hole wave functions. As one of the charge carriers (electron or hole) is located in the shell, an over growth of type II CSNCs with an outer shell of an appropriate material which can be used in the same way as in type I systems to improve the fluorescence QY and photo stability.

1.7. Quantum confinement in semiconductor nanoparticles

A semiconductor nanocrystal (SNC) or quantum dot (QD) is a semiconductor whose excitons are confined in all the three spatial dimensions. As a result, they have properties that are between those of bulk semiconductors and those of discrete molecules. Size effects are observed in semiconductor crystals measuring 10-100 nm whereas quantum size effects are usually characteristics of nanocrystallites measuring less than 10 nm. In fact, the properties of nanocrystalline particles differ from those of bulk materials. The high surface area to volume ratio results in as many atoms at the surface as in the crystalline lattice and the electronic bands are split up in to discrete energy levels as a result of three dimensional confinement of the charge carriers. This quantum confinement of charge results in an increase in the bandgap with decreasing particle size. The quantum confinement effect in low dimensional semiconductor systems was described earlier [52,53]. The bulk crystalline structure is preserved in a nanocrystal. However, due to
quantum confinement, nanocrystals have molecule-like discrete electronic states which exhibit strong size dependent properties. In the last decade, comprehensive investigations were made to explore size dependent properties of semiconductors with the emphasis on optical properties, including absorption and luminescence [54-56].

Detailed knowledge of the optical properties of the nanostructured materials is important for understanding of the photophysical and photochemical process that follow the absorption of light quanta. Steigewald and Brus [57] used quantum mechanical molecular orbital calculations to explain the quantum confinement effect on optical absorption, accounting for the well established blue shift in the absorption spectra with decreasing particle size. Bawendi [58] has also provided a overview of this field. As a means of explaining observed spectral shifts during the early stages of inorganic semiconductor particle growth, molecular orbital (MO) and linear combination of atomic orbital coupled with molecular orbital (LCAO-MO) procedures provide information for the construction of energy level diagrams for clusters of several molecules up to size characteristic of bulk semiconductor. Increasing the number of molecules in a cluster requires the addition of filled and empty orbitals to the energy manifold. This decreases the energy differences between the filled orbitals as well as the empty orbitals. The energy gap between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) is also observed to decrease.

For a bulk semiconductor, the filled and empty state form separated continuums i.e., the valence and conduction bands. In the quantum size regime, the energy levels within the filled and the empty states remain discrete and the bandgap between the HOMO and the LUMO states
increases, compared to the bulk materials, as shown in the schematic diagram, Fig.1.11. The bandgap $E_g$, increases in magnitude as the semiconductor particle radius decreases in size to the point where it becomes comparable or smaller than the exciton radius. These properties lead to the applications in a wide range of fields i.e., semiconducting quantum well, superlattice devices, nonlinear optical materials, photocatalysis and imaging systems.

For II-VI compounds, the maximum radii for the onset of quantum confinement effect (Q-size effects) leading to the enhancement of bandgap have been determined by Bawendi [58] to be 10 to 100 Å. Wide band photoconductors such as, TiO$_2$ (rutile) and ZnO undergo increase in bandgap as radii approach in the range of 50 Å. It is interesting to note that a blue shift in the long wavelength optical absorption edge with decrease in particle size was first observed by Berry [59] for AgBr samples with radii of 65Å and 350Å. Quantum confinement effects in semiconductor nanocrystals are known to make their optical and electrical properties significantly different from those of the bulk material, particularly when the physical dimensions are reduced close to the characteristic length known as the exciton Bohr diameter.

The characteristic lengths are usually in the range of few nanometers when the material exhibits size dependent optical and electrical properties. One of the most important consequences of the spatial confinement effect is an increase in the energy of the band to band exciton peaks (blue shift) as the radius of a microcrystallite semiconductor is reduced in relation with the Bohr radius.
Fig. 1.11 A schematic diagram of the molecular orbital model for bandstructure
Theoretically, the regime of quantum confinement which are experimentally interesting differ in their main electron-hole interaction energy, that is, the Coulomb term and the confinement energy of the electron and hole and the kinetic energy [52].

1.7.1 Weak confinement regime

To observe this regime, the radius of a crystallite should be greater than the bulk exciton Bohr radius $a_B$. In this region of weak confinement, the dominant energy is the Coulomb term and there occurs a size quantization of the exciton motion. The exciton energy states are shifted to higher energies by confinement and the shift in energy $\Delta E$ is proportional to $1/R^2$. The shift, $\Delta E$, of the exciton ground state is given approximately by

$$\Delta E \approx \frac{\hbar^2 \pi^2}{2MR^2}$$  \hspace{1cm} (1.5)

where $M$ is the mass of the exciton, given by $M = m_e^* + m_h^*$ with $m_e^*$ and $m_h^*$ being the effective masses of the electron and hole respectively [60].

1.7.2 Moderate confinement regime

The moderate confinement regime occurs when $R \approx a_B$ and $a_h < R < a_e$, where $a_h$ and $a_e$ are the hole and electron Bohr radii respectively. This region is well observable in small QDs in II-VI semiconductors. Its characteristic feature is the well restricted motion of a photoexcited hole.
1.7.3 Strong confinement regime

Finally, the size of a QD can be decreased in such a way that \( R << a_B, R << a_h \) and \( a_e \), in the strong confinement regime. The Coulomb term of electron-hole interaction is now small and can now be ignored or treated as perturbation. The electrons and holes can now be thought of as confinement independent particles. So excitons are not formed and separate size quantization of an electron and hole is the dominant factor. The optical spectra should then consist of a series of lines due to transition between sub-bands. This factor was confirmed experimentally and the simple model gives the shift in energy as a function of crystallite size as,

\[
\Delta E \approx \frac{\hbar^2 \pi^2}{2\mu R^2}
\]

in which the exciton mass \( M \) is replaced by reduced exciton mass \( \mu \) as,

\[
\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}
\]

The electrons and holes in QDs are treated as independent particles and for the excited state there exist a ladder of discrete energy levels as in molecular systems [61].

1.8 Applications of semiconductors

The high breakdown voltage of wide bandgap semiconductors is an important property in high-power applications that require large electric fields. Devices for high power and high temperature applications have been developed [30]. Both gallium nitride and silicon carbide are robust materials well suited for such applications. Cubic boron nitride is used as
quantum well. Most of them are applied in space programmes and military systems. They have not begun to displace silicon from its leading place in the general power semiconductor market. In fact, the resistivity of semiconductors varies with temperature. This enables semiconductors to be used as thermometers. Through doping the appropriate sensitivity in the required ranges can be obtained [62]. The strength of magnetic field can be measured using Hall voltage technique.

Optoelectronic devices are capable of sensing or responding to light of various wavelengths. This is due to the phenomenon of photoconductivity whereby a semiconductor can greatly increase its electrical conductivity if the radiation has sufficient energy to promote electrons across the bandgap. Different suitable bandgap can be used for different applications.

1.8.1 Applications of III-V semiconductors

**Aluminium nitride**

Aluminium nitride is a nitride of aluminium. Its wurtzite phase (w-AlN) is an extremely wide bandgap (6.2 eV) semiconductor material which has potential application for deep ultraviolet electronics.

**Aluminium phosphide**

Aluminium phosphide (AlP) is a compound of aluminium and phosphorus. AlP is used in semiconductor industry as a semiconductor material, usually combined with other elements to make more stable semiconductor alloys for application in devices such as light emitting diode. e.g. aluminium gallium indium phosphide. Solar cells can be fabricated from boron arsenide.
Gallium arsenide

Gallium arsenide (GaAs) is a compound of two elements, Gallium and Arsenic. It is an important semiconductor and is used to make devices such as microwave frequency integrated circuits, infrared light emitting diodes, laser diodes and solar cells.

Gallium nitride

Gallium nitride (GaN), when doped with a suitable transition metal such as manganese, is a promising spintronics material (magnetic semiconductor). Resonant Tunnelling Diode is made from III-N material and it has a useful property such a negative differential resistance.

Indium antimonide

Indium antimonide (InSb) is a narrow gap semiconducting material from III-V groups used in infrared detectors, including thermal imaging cameras, FLIR system, infrared homing missile guidance systems and infrared astronomy.

Indium nitride

Indium nitride (InN) is a direct narrow bandgap semiconductor (~0.7eV at room temperature), with potential in high speed opto-electronics and solar cells. When combined with gallium to produce the ternary alloy InGaN the bandgap is tunable over the range 0.7 - 3.4 eV, from the infra-red to the ultraviolet, encompassing the entire visible spectrum [63]

Indium phosphide

Indium phosphide (InP) is a binary semiconductor composed of indium and phosphorus. It is used in high power and high frequency
electronics because of its superior electron velocity with respect to the more common semiconductors such as silicon and gallium arsenide. In an effort to incorporate magnetism into existing semiconductor structures, a magnetic dopant (Cr, Mn, Fe, Ni, Co, Gd) is included into the material during growth. The exchange coupling between these dopants leads to magnetic properties.

1.8.2 Applications of II-VI semiconductors

Cadmium telluride

Cadmium telluride (CdTe) is a crystalline compound formed from cadmium and tellurium. It is used as an infrared optical window and a solar cell material. It is usually sandwiched with cadmium sulfide to form a p-n junction photovoltaic solar cell. Typically, CdTe n-i-p structure is used to make thin film solar cells. Cadmium is abundant, produced as a by-product of other important industrial metals such as zinc, consequently it has not had the wider price swings that have happened in the past two years with silicon prices [64].

Cadmium selenide

Cadmium selenide is a solid, binary compound of cadmium and selenium. Common names for this compound are cadmium (II) selenide, cadmium selenide and cadmoselite. This material is transparent to infrared (IR) light, and has seen limited use in windows for instruments utilizing IR light. CdSe is also being developed for use in optoelectronic devices, laser diodes, nanosensing and biomedical imaging. CdSe is also being developed for use in opto-electronic devices, laser diodes, nanosensing, and biomedical imaging [65]. They are also used being tested for use in high-efficiency solar cells [66].
Cadmium sulfide

Cadmium sulfide is a chemical compound with the formula CdS. It is yellow in colour and is a semiconductor [67]. It exists in nature as two different minerals, hexagonal greenockite [68] and cubic hawleyite [69]. Cadmium sulfide is a direct bandgap semiconductor (2.42 eV) [70] and has many applications for example in light detectors. CdS is used as pigment in plastics [71].

Zinc telluride

Zinc telluride is the chemical compound with the formula ZnTe. This solid is an intrinsic semiconductor material with bandgap of 2.23–2.25 eV. It is usually a p-type semiconductor. Its crystal structure is cubic like that for sphalerite and diamond. It can be used for solar cells. Its lattice constant is 0.61034 nm, allowing it to be grown with or on aluminium antimonide, gallium antimonide, indium arsenide and lead selenide. With some lattice mismatch, it can also be grown on other substrates such as GaAs and it can be grown in thin-film polycrystalline form on substrates such as glass in the manufacture of thin-film solar cells [72].

Zinc oxide

Zinc oxide is an inorganic compound with the formula ZnO. It usually appears as a white powder, nearly insoluble in water. The powder is widely used as an additive into numerous materials with some products including plastics, ceramics, glass, cement, rubber (e.g. car tyres), lubricants, paints, ointments, adhesives, sealants, pigments, foods, batteries, ferrites, fire retardants, first aid tapes and so on [73].
**Zinc selenide**

Zinc selenide is a light yellow binary solid compound. It is an intrinsic semiconductor with a bandgap of about 2.82 eV at 25°C. ZnSe rarely occurs in nature. ZnSe doped with chromium (ZnSe: Cr) has been used as an infrared laser gain medium emitting at about 2.5 µm [74].

**Zinc sulfide**

Zinc sulfide is a chemical compound with the formula ZnS. It is a white to yellow-colored powder or crystal. It is typically encountered in the more stable cubic form known as zinc blende or sphalerite. Zinc sulfide, with addition of few ppm of suitable activator, is used as phosphor in many applications, from cathode ray tubes through x-ray screens to glow in the dark products [75]. The hexagonal form is known both as a synthetic material and as the mineral wurtzite [76]. Both sphalerite and wurtzite are intrinsic wide-bandgap semiconductors. Copper-doped zinc sulfide is used in electroluminescent panels [77]. It also exhibits phosphorescence due to adding impurities on illumination with blue or ultraviolet light. The Fig.1.12 compares the lattice constant to bandgap of many compounds.

**1.9 Effective mass approximation**

An electron in a crystal may behave as if it had a mass different from the free electron mass $m_0$. There are crystals in which the effective mass of the carriers is much larger or much smaller than $m_0$. The effective mass may be anisotropic and it may even be negative. The important point is that the electron in a periodic potential is accelerated relative to the lattice in an applied electric or magnetic field as if its mass is equal to an effective mass. It is usually denoted by $m^*$. 
Fig. 1.12 Variation of bandgap with a lattice constant for many semiconductor compounds
The difference in effective mass between the two semiconductor materials affects the transport of electrons in parallel plane interfaces with an effective mass

\[
\frac{1}{m^*} = \frac{P}{m_1} + \frac{(1-P)}{m_2}
\]  

(1.8)

where \( m_1 \) and \( m_2 \) are the effective mass of electron in the well region and in the barrier respectively, \( P \) is the probability of the electron existence inside the well and \( 1-P \) its probability in the quantum barrier [78]. The effective mass variation produces a change in boundary condition also.

This change in effective mass of the electron across the interface changes the apparent height \( V_0 \) of the potential barrier in which the kinetic energy of the electron depends. And it is given as

\[
\tilde{V}_0 = V_0 - \Delta
\]

(1.9)

where

\[
\Delta = E \left( 1 - \frac{m_1}{m_2} \right)
\]

(1.10)

where \( m_1 \) and \( m_2 \) are as described earlier and \( E \) is the electron energy. The calculation of static energy levels within quantum wells should account for the variation in the effective mass across the hetero junctions [79-81].

Since the earliest work of Conley et al., [82] and Ben Daniel and Duke [83] who derived the boundary conditions on solutions of the envelope functions as

\[
\psi(z) and \frac{1}{m^*} \frac{\partial}{\partial z} \psi(z)
\]

(1.11)
on considering the electron transport across the heterojunction. These boundary conditions have become known as the Ben Daniel-Duke boundary conditions.

The effective mass approximation is applied to a wide variety of calculations of the electronic properties of semiconductors, such as, shallow impurity states, transport properties, optical properties and so on. The perturbing potential, \( H_1(r) \), varies very slowly compared with the lattice constant \( a \). Hence the effective mass equation can be simplified based on a single band. The Schrödinger equation for the one electron Hamiltonian is written as

\[
[H_0 + H_1(r)]\psi(r) = E\psi(r) \quad (1.12)
\]

and

\[
H_0 = \frac{p^2}{2m^*} + V(r) \quad (1.13)
\]

where \( p \) is the momentum of the electron. The solution of the above equation is written as,

\[
\left[-\frac{\hbar^2}{2m^*}\nabla^2 + H_1(r)\right]F(r) = EF(r) \quad (1.14)
\]

on substituting \( p = -i\hbar\nabla \), the quantum mechanical operator for momentum. Therefore, the energy of the electron \( E \) is assumed to be expressed in terms of the wave vector \( k \) as

\[
E(k) = \frac{\hbar^2 k^2}{2m^*} \quad (1.15)
\]

The above Eq.(1.15) is called effective mass equation and this approximation is called effective mass approximation [84].
Experimental measurements of the effective mass have revealed it to be isotropic as might be expected since the crystal potential along [001] axis is different from along [111] axis. Adachi [85] reported the values for GaAs and its alloys. Thus, the electronic states are given by the relation of electron energy as a function of electron wave vector $k$ and the electron energy $E(k)$. In considering electron transport, the electrons occupy mainly the states near the conduction band minimum in thermal equilibrium. Thus, the electrons are well described by Eq.(1.15).

### 1.10 Variational principle

The Hamiltonian $H$ with basis $|n\rangle$, for arbitrary $|\psi\rangle$

$$
\langle \psi | H | \psi \rangle = \sum_n \langle \psi | n \rangle \langle n | H | \psi \rangle = \sum_n E_n \langle \psi | n \rangle \langle n | \psi \rangle
$$

$$
\geq E_0 \sum_n |\langle \psi | n \rangle|^2 = E_0 \langle \psi | \psi \rangle
$$

and

$$
E_0 \leq \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \tag{1.16}
$$

The Ritz variational principle consists in specifying $|\psi(\mu)\rangle$ be a function of one or more parameters $\mu$ and the expression for the upper bound ground state energy $E(\mu)$ is given by

$$
E(\mu) = \frac{\langle \psi(\mu) | H | \psi(\mu) \rangle}{\langle \psi(\mu) | \psi(\mu) \rangle}. \tag{1.17}
$$

In this procedure, an error in the wave function is obviously itself at quadratic order in the energy, i.e.
\[ |\psi\rangle = |n\rangle + |\epsilon\rangle \]  

(1.18)

with \( \langle n | \epsilon \rangle = 0 \); then

\[
\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{E_n + \langle \epsilon | H | \epsilon \rangle}{\langle n | n \rangle + \langle \epsilon | \epsilon \rangle} = E_n + O(\epsilon^2)
\]

(1.19)

The energy is determined more accurately than the wave function under the application of a variational principle.

The variational principle is an important tool in mathematical physics in the proof of exact inequalities.

**1.11 Perturbation method**

The Perturbation theory is concerned with finding the changes in the energy levels and eigen functions of a system when a small disturbance is applied. In this case, the Hamiltonian is broken into two parts, one of which is large (\( H^0 \)) and represents a system for which the Schrödinger equation can be solved exactly while the other part is small and can be treated as perturbation term (\( H' \)) [86].

The Schrödinger equation is

\[ H \psi = E \psi. \]

(1.20)

Writing the Hamiltonian into two parts,

\[ H = H^0 + H. \]

(1.21)

Expanding the total Hamiltonian, \( H \), the energy, \( E \) and the wave function \( \Psi \), in terms of some parameter \( \lambda \), as

\[ H^0 + \lambda H' + \lambda^2 H'' + \lambda^3 H''' + \ldots \]

(1.22)
\[ E^0 + \lambda E' + \lambda^2 E'' + \lambda^3 E''' + \ldots \]  
\[ \psi^0 + \lambda \psi' + \lambda^2 \psi'' + \lambda^3 \psi''' + \ldots \]

where the primed quantities represent their corresponding orders of perturbations respectively.

Substituting in the Schrödinger equation,

\[
(H^0 + \lambda H' + \lambda^2 H'' + \lambda^3 H''' + \ldots) (\psi^0 + \lambda \psi' + \lambda^2 \psi'' + \lambda^3 \psi''' + \ldots) =
\]

\[
(E^0 + \lambda E' + \lambda^2 E'' + \lambda^3 E''' + \ldots) (\psi^0 + \lambda \psi' + \lambda^2 \psi'' + \lambda^3 \psi''' + \ldots).
\]

(1.25)

On collecting the coefficients of like powers of \( \lambda \) and limiting the total Hamiltonian, \( H \) upto \( \lambda H' \), the first order perturbation energy is obtained by equating the coefficient of \( \lambda \) and is given as,

\[
E_k' = \int \psi_k^{0*} H' \psi_k^0 d\tau
\]

(1.26)

where the \( \psi_k^{0*} \) over the wave function represents the conjugate form of the wave function. And the first order wave function is given as

\[
\psi_k' = \psi_k^0 + \sum_{l \neq k} \frac{\langle l | H' | k \rangle}{E_k^0 - E_l^0} \psi_l^0
\]

(1.27)

where \( k, l \) represent different wave function states.

1.12 Optical properties of semiconductor

Quantum size effects have been observed experimentally for many nanocrystalline semiconductors [87]. The optical absorption spectrum of a nanocrystalline semiconductor provides an accessible and
straightforward method for the evaluation of quantum size effects. The absorption of a photon, leading to excitation of an electron from the valence band to the conduction band, is associated with the bandgap energy ($E_g$). The absorption of photons with energy similar to that of the bandgap, $hv \geq E_g$, leads to an optical transition producing an electron in the conduction band of the semiconductor along with a hole in the valence band. Absorption of photons with energy much greater than $E_g$ leads to excitations above the conduction band edge, these electrons can lose the excess energy by radiation-less processes.

### 1.12.1 Absorption Coefficient

The absorption coefficient determines how far into a material light of a particular wavelength can penetrate before it is absorbed. In a material with a low absorption coefficient, light is only poorly absorbed, and if the material is thin enough, it will appear transparent to that wavelength. The absorption coefficient depends on the material and also on the wavelength of light which is being absorbed. Semiconductor materials have a sharp edge in their absorption coefficient since light which has energy below the bandgap does not have sufficient energy to excite an electron into the conduction band from the valence band. Consequently this light is not absorbed.

Different semiconductor materials have different absorption coefficients:

- Materials with higher absorption coefficients more readily absorb photons which excite electrons into the conduction band.
- The absorption coefficients of materials aid engineers in determining which material to use in their solar cell designs.
The absorption ($A$) of light by a semiconductor material with thickness $l$ can be expressed as

$$A = \alpha l \quad (1.28)$$

where, $\alpha$ represents the absorption coefficient of the solid and is a function of the radiation frequency.

All electronic transitions are subject to selection rules, for semiconductors the requirement (besides $hv \geq E_g$) that the wave vector $k$, should be conserved. $k_{photon}$ is small when compared with the wave vectors of the electron before ($k_e$) and after excitation ($k_e'$).

$$k_e + k_{photon} = k_e' \quad (1.29)$$

$$k_e = k_e' \quad (1.30)$$

The absorption coefficient for a photon of a given energy is proportional to the probability ($P_{if}$), the density of states in the initial state ($n_i$) and the density of available final states ($n_f$). This process must be summed for all possible transitions between states separated by an energy difference equal to the energy of the incident photon.

$$\alpha(hv) \propto \Sigma P_{if} n_i n_f. \quad (1.31)$$

Semiconductors in which there is conservation of the wave vector for optical transitions are referred to as direct bandgap semiconductors and have large absorption coefficients. A useful expression relating the absorption coefficient and the photon energy of a direct transition near the threshold is given by equation [88],

$$\alpha(hv) \propto (E_g - hv)^{1/2} \quad (1.32)$$
The bandgap energy of a nanocrystalline semiconductor can be experimentally estimated from its optical spectrum and by using Eq.(1.32). Experimentally quantum size effects are observed as a shift towards higher energy values for the band edge (a blue shift), as compared to the typical value for the corresponding macrocrystalline material. Nanocrystalline samples often show a peak in the optical spectra at room temperature. The absorption of electromagnetic radiation by nanocrystallite material is relatively straightforward but the luminescent behavior of such particles is more complicated. And the ideas that have emerged for explaining these phenomena illustrate an interesting interplay between experimental works and theoretical approach.

Fig.1.13 predicts photons which have energy above the bandgap, the absorption coefficient is not constant, but still depends strongly on wavelength. The probability of absorbing a photon depends on the likelihood of having a photon and an electron interact in such a way as to move from one energy band to another. Photons which have energy very close to that of the bandgap, the absorption is relatively low since only those electrons directly at the valence band edge can interact with the photon to cause absorption. As the photon energy increases, not just the electrons already having energy close to that of the bandgap can interact with the photon. Therefore, a larger number of electrons can interact with the photon resulting in the photon being absorbed.
Fig. 1.13 Absorption Coefficient as a function of wavelength for various semiconductors
1.12.2 Refractive index

Refractive index is used to measure how fast the light propagates through a medium. Such media must be poor conductors and are usually called dielectric media. The Kramers Kronig relations, together with a modelisation of the imaginary part of the dielectric function, allow a phenomenological model of the refractive index. Assuming the imaginary part of the dielectric function, $\varepsilon''$, with the form,

$$\varepsilon''(E) = \eta E$$ \hspace{1cm} (1.33)

with $\eta > 1$, between the bandgap energy $E_g$ and a final cutoff energy $E_f$ and zero. Because the dielectric response of the III-V materials cannot be easily represented by a finite sum of oscillators.

From an integration of the Kramers-Kronig equation, the refractive index is obtained as,

$$n^2(E) = 1 + \frac{\eta}{2\pi} (E_f^4 - E_g^4) + \frac{\eta}{\pi} E^2 (E_f^2 - E_g^2)$$

$$+ \frac{\eta}{\pi} E^4 \ln \left( \frac{E_f^2 - E^2}{E_g^2 - E^2} \right)$$ \hspace{1cm} (1.34)

where $\eta$, $E_f$ and $E_g$ fully characterize the material.

$$\varepsilon'(E) = 1 + \frac{E_{oe} E_d}{E_{oe}^2 - E^2}$$ \hspace{1cm} (1.35)

These parameters are related to the ones of our model through

$$E_f = \sqrt{2E_{oe}^2 - E_g^2}$$ \hspace{1cm} (1.36)
and

\[ \eta = \frac{\pi}{2} \frac{E_d}{E_{oe}^3 (E_{oe}^2 - E_g^2)} \]  

(1.37)

1.12.3 Oscillator strength

An atom or a molecule can absorb light and undergo a transition from one quantum state to another. The oscillator strength is a dimensionless quantity to express the strength of the transition. The oscillator strength (directly proportional to the absorption coefficient) increases as particle size decreases as a result of strong overlapping of the wave functions of confined charge carriers [87]. Such effects were clearly demonstrated in a study of CdS nanocrystallites with different and well-defined size distributions [89]. Decreasing the size of the CdS particles leads not only to a shift in the excitonic peak to higher energy but also to an increase in the molar absorption coefficient.

1.13 Excitons

Exciton is the combination of an electron and a positive hole, which is free to move through a nonmetallic crystal as a unit. Because the electron and the positive hole have equal but opposite electrical charges, the exciton as a whole without net electrical charge. This makes exciton difficult to detect, but detection is possible by indirect means. When an electron in an exciton recombines with a positive hole, the original atom is restored and the exciton vanishes. The energy of the exciton may be converted into light when this happens, or it may be transferred to an electron of a neighbouring atom in the solid. If the energy is transferred to a neighbouring electron, a new exciton is produced as this electron is forced away from its atom.
To understand the quantum mechanical behavior of a semiconductor particle, consider an electron which is promoted to the conduction band from the valence band as shown in Fig. 1.14. Left behind in the valence band is a hole, which can be thought of as a particle with its own charge (+1) and effective mass. The electron and hole are considered bound to each other via Coulombic attraction and this quasiparticle is then known as an exciton. The exciton can be considered as hydrogen like system and a Bohr approximation of the atom can be used to calculate the spatial separation of the electron-hole pair of the exciton by

\[ a_B = \varepsilon h^2 / \pi \mu e^2 \]

(1.38)

where \( a_B \) is the radius of the sphere, \( \varepsilon \) is the dielectric constant of the semiconductor, \( \mu \) is the reduced mass of the electron-hole pair, \( h \) is Planck’s constant and \( e \) is the charge on the electron. For many semiconductors, the masses of the electron and hole are determined by ion cyclotron resonance.

The size dependent optical properties of nanoparticles are examples of the size quantization effect which occurs when the size of the nanoparticle is smaller than the bulk-exciton Bohr radius, \( a_B \), of the semiconductor [90].

\[ l < < R \leq a_B \]

(1.39)

The above Eq.(1.39) defines, for a spherical crystallite of radius, \( R \), the region of intermediate character between that of a molecule and that of the bulk material (\( l \) is the lattice spacing).
Fig. 1.14 Bound energy level of the exciton
Charge carriers, in semiconductor nanocrystallites, are confined within three dimensions by the crystallite. In the case of ideal quantum confinement, the Bloch type wave function is given by

$$\psi(r) = \phi(Kr)u(r) \quad (1.40)$$

has to satisfy the boundary conditions of

$$\psi(r \geq R) = 0 \quad (1.41)$$

For nanoparticles, the electron and hole are closer together than in the macrocrystalline material and as such the Coulombic interaction between electron and hole cannot be neglected. Moreover, they have higher kinetic energy than in the macrocrystalline material. On the basis of the effective mass approximation, Brus [53] showed for CdE (E = S or Se) nanocrystallites that the size dependence on the energy of the first electronic transition of the exciton (or the bandgap shift with respect to the typical bulk value) can be approximately calculated using

$$\Delta E \approx \frac{\hbar^2 \pi^2}{2R^2} \left[ \frac{1}{m^*_{e}} + \frac{1}{m^*_{h}} \right] - \frac{1.8e^2}{R}. \quad (1.42)$$

Eq.(1.42) is an analytical approximation for the first electronic transition of an exciton which can be described by a hydrogenic Hamiltonian. In Eq.(1.42), the Coulomb term shifts the first excited electronic state to lower energy, R-1, while the quantum localization terms shift the state to higher energy, R-2. Consequently, the first excitonic transition (or bandgap) increases in energy with decreasing particle diameter. Thus, the corresponding Hamiltonian is given by,
This prediction has been confirmed experimentally for a wide range of semiconductor nanocrystallites, with a blue shift in the onset of the absorption of light being observed with decreasing particle diameter [87]. Moreover, the valence and conduction bands in nanocrystalline materials consist of discrete sets of electronic levels and can be viewed as a state of matter between that of molecular and the bulk material. Eq.(1.42) does not account for a number of other important effects observed in real nanocrystallites, such as the coupling of electronic states and effects attributable to surface structure [91]. The constants used in the model (the effective masses and the dielectric constants) are those for macrocrystalline solids. The model is not quantitatively accurate with calculations deviating from experimental values, especially for very small nanocrystallites. In such particles, the first electronic transition is located in a region of the energy band in which the normal effective mass approximation is not valid. Although Eq.(1.42) is not valid for all types of semiconductors, from a practical point of view, this model is particularly useful and the size-dependent energy shift for a number of nanocrystalline semiconductors can be estimated. Furthermore, the model also provides a useful qualitative understanding of the quantum confinement effects observed in semiconductor nanocrystallites.

1.13.1 Classification of exciton
1.13.1.1 Frenkel exciton

Frenkel exciton has a small dielectric constant but the Coulomb interaction between an electron and a hole may be strong and the excitons thus tend to be small of the same order as the size of the unit cell. Molecular excitons may even be entirely located on the same molecule,
as in fullerenes. This Frenkel exciton, named after Ya kov Frenkel, has a
typical binding energy on the order of 0.1 to 1 eV as shown in Fig1.15.
Frenkel excitons are typically found in alkali halide crystals and in
organic molecular crystals composed of aromatic molecules such as
anthracene and tetracene [92].

1.13.1.2 Wannier-Mott exciton

In semiconductors, the dielectric constant is generally large.
Consequently, electric field screening tends to reduce the Coulomb
interaction between electrons and holes. The result is a Wannier exciton
[93] which has a radius larger than the lattice spacing. As a result, the
effect of the lattice potential can be incorporated into the effective masses
of the electron and hole. Likewise, because of the lower masses and the
screened Coulomb interaction, the binding energy is usually much less
than that of a hydrogen atom, typically on the order of 0.01eV. Wannier-
Mott excitons are typically found in semiconductor crystals with small
energy gaps and high dielectric constants but have also been identified in
liquids, such as liquid xenon.

1.13.2 Optical transitions of excitons in quantum dots

Optical transitions in QDs are associated with their electronic
states. Quantum size effects that are very well predicted by the particle-
in-box model can be also observed in absorption spectroscopy. The
absorption bands shift to higher energies with decreasing quantum dot
radius. It can be seen that the optical bandgap is blueshifting dramatically
from the bulk size value to the quantum sizes, as shown in Fig1.16, for
the CdSe with bulk value of the optical bandgap at the 716 nm (~1.68
eV).
Fig. 1.15 Frenkel and Wannier-Mott excitons

**Wannier exciton** (typical of inorganic semiconductors)

**Excitons**
(bound electron-hole pairs)

**Frenkel exciton** (typical of organic materials)

**SEMICONDUCTOR PICTURE**

- Conduction band
- Valence band

**GROUND STATE**

**WANNIER EXCITON**

*binding energy ~10 m eV
radius ~100 Å*

**MOLECULAR PICTURE**

**GROUND STATE**

**FRENKEL EXCITON**

*binding energy ~1 eV
radius ~10 Å*

**Charge Transfer (CT) Exciton** (typical of organic materials)

- *treat excitons as chargeless particles capable of diffusion.*
- *also view them as excited states of the molecule*
Fig. 1.16 Single-particle picture and two-particle (Excitons) picture of bulk semiconductors
The absorption spectrum for a quantum dot of 115 Å in size is broad and featureless, characteristic to the bulk absorption spectrum. Below exciton Bohr radius the absorption spectra exhibit a fine structure. Appearance of a fine structure in absorption spectrum is due to the presence of the discrete energy levels.

1.13.3 Selection rules for optical transitions

An exciton is formed by an electron and hole, i.e. by two fermions having projections of the angular momenta on a given axis equal to \( m_j^e = m_j^h = \pm 1/2 \); for an electron in the conduction band with s-symmetry and \( m_j^h = \pm 1/2, \pm 3/2 \) for a hole in the valence band with p-symmetry (in zinc-blend semiconductor crystals). The states with \( m_j^h = \pm 1/2 \) and \( m_j^h = \pm 3/2 \) are called light hole and heavy hole states, respectively. In the bulk samples, at \( \mathbf{k} = 0 \) the light and heavy hole states are degenerated. Strain in the crystal and/or confinement of the carriers by a potential will break the degeneracy of the VB states. Selection rules for direct interband optical transitions in zinc-blende semiconductors with the quantization axis along the growth direction are shown in Fig.1.17.

When a layer exhibits a compressive strain in the plane of the layer, the conduction band will move to a higher energy. Meanwhile, the heavy hole and the light hole bands become nondegenerate at \( \mathbf{k} = 0 \), with the heavy hole band being the topmost one. In the case of tensile strain all the three bands mentioned above move in opposite directions compared to the case of compressive strain. Thus, compressive strain acts in the same sense as the effect of the quantum confinement on the shifting of the valence bands. Therefore, the HH exciton formed by an electron and a heavy hole is energetically favoured.
Fig. 1.17 Radiative interband transitions allowed by the selection rules for zinc blend semiconductors with the quantization axis along the growth direction. The labels near the arrows indicate the relative transition intensities and polarization of the light [94]
The total exciton angular momentum $J$ has the following projections on the quantization axis: $m_{j}^{x} = \pm 1, \pm 2$. The projection of the photon spin is 0 or $\pm 1$ and that the spin is conserved in the processes of photo-absorption, the excitons with spin projections $m_{j}^{x} = \pm 2$ cannot be optically excited and do not participate in the emission. These are so called spin-forbidden or dark states. The conservation of spin in the photo-absorption allows spin-orientation of the excitons due to absorption of polarized excitation light (i.e. optical orientation), the effect which manifests itself in the polarization of photoluminescence. $\sigma^{+}$ and $\sigma^{-}$ circularly polarized light excites $| -1/2; +3/2 \rangle$ and $| +1/2; -3/2 \rangle$ excitons, respectively (assuming direct excitation and no spin loss). Linearly-polarized light excites a linear combination of $+1$ and $-1$ exciton states, so that the total exciton spin projection on the quantization axis is zero in this case.

All finite quantum wells have definite parities for the envelope wave functions due to the quantum confinement states of a symmetric. It is well known that the parity-selection rule requires that the two states must have the same parity. It has been shown that some parity allowed but orthogonality forbidden transitions such as $n=3$ heavy hole state to $n=1$ electron state transition are in general weakly allowed transitions for finite barrier quantum well structures without any consideration of band mixing, non-parabolicity or even imperfections of the symmetric potential. Since any finite quantum well has a large differences in their effective masses (electron and hole effective mass) and the barrier heights, the allowed transitions for symmetric will affect the spreading of the wave functions. However, the strongest transitions are those $\Delta n = 0$ selection rules. The overlap integral between such wave functions is maximum [95].
1.14 Cadmium telluride

Cadmium telluride (CdTe) is a crystalline compound formed from cadmium and tellurium. It is used as an infrared optical window and a solar cell material. It is usually sandwiched with cadmium sulfide to form a p-n junction photovoltaic solar cell.

1.14.1 Properties of cadmium telluride

Cadmium telluride is one of the most promising II–VI semiconductor compounds for any electronic and optoelectronic devices because of its optical and transport properties. The high absorption coefficient (>10⁴cm⁻¹) of the material in the visible and near IR region of the solar spectrum and the direct bandgap close to the optimum value for efficient solar energy conversion makes it ideal for solar cell fabrication [96]. Cadmium telluride typically has a cubic (sphalerite, or zincblende) as shown in Fig.1.18a. CdTe semiconductor used for high energy radiation detectors covering the energy range from keV to MeV [97-101].

In practical use of CdTe in the manufacture of room temperature X- and γ-ray detectors, the semiconductor must be high electrical resistivity material in order to provide a low leakage current, extended depletion region and high efficiency of a device. CdTe-based detectors have usually been developed as a diode structure with blocking contacts (Schottky barrier) [98-105] or electrical junctions (p-i, n-i, p-i-n or p-n) formed in the surface region of crystals [101].
Fig. 1.18a Crystal structure of CdTe
Fluorescence spectra of colloidal CdTe quantum dots of various sizes increase approximately from 2 to 20 nm.

The blue shift of fluorescence is due to quantum confinement. Bulk CdTe is transparent in the infrared, from close to its bandgap energy (1.44 eV at 300K). Fig 1.18b corresponds to infrared wavelength about 860 nm) out to wavelengths greater than 20µm correspondingly, CdTe is fluorescent at 790 nm as shown in Fig.1.18c. When the size of CdTe crystal is being reduced to a few nanometers and below, thus making a CdTe quantum dot, the fluorescence peak shifts towards through the visible range to the ultraviolet. CdTe has very low solubility in water. It is etched by many acids including hydrochloric and hydrobromic acid, forming (toxic) hydrogen telluride gas and toxic cadmium salts. It is a reducing agent and is unstable in air at high temperatures. Cadmium telluride is commercially available as a powder, or as crystals. It can be made in to nano crystals [106].

1.14.2 Application of cadmium telluride

CdTe can be alloyed with mercury to make a versatile infrared detector material (HgCdTe). CdTe alloyed with a small amount of zinc makes an excellent solid-state X-ray and gamma ray detector (CdZnTe). CdTe is used as an infrared optical material for optical windows and lenses but it has small application and is limited by its toxicity. CdTe is also applied for electro-optic modulators.
Fig.1.18b  Band structure of CdTe

Fig.1.18c  Optical and electronic properties
It has the greatest electro-optic coefficient of the linear electro-optic effect among II-VI compound crystals \((r_{41}= r_{52}= r_{63} = 6.8 \times 10^{-12}\text{m/V})\). CdTe doped with chlorine is used as a radiation detector for x-rays, gamma rays, beta particles and alpha particles.

CdTe can operate at room temperature allowing the construction of compact detectors for a wide variety of applications in nuclear spectroscopy. The properties that make CdTe superior for the realization of high performance gamma- and x-ray detectors are high atomic number, large bandgap and high electron mobility \(\sim 1100\text{cm}^2/\text{V.s}\) which results in high intrinsic \(\mu\tau\) (mobility-lifetime) product and therefore high degree of charge collection and excelent spectral resolution [107].

**1.15 Zinc telluride**

Zinc telluride is a binary chemical compound with the formula ZnTe. This solid is a semiconductor material with bandgap of 2.23–2.25eV. It is usually a p-type semiconductor. Its crystal structure is cubic, like that for sphalerite and diamond.

**1.15.1 Properties of zinc telluride**

ZnTe has the appearance of grey or brownish-red powder, or ruby-red crystals when refined by sublimation. Zinc telluride typically has a cubic (sphalerite, or zincblende) crystal structure as shown Fig 1.19a, but can be also prepared as hexagonal crystals (wurzite structure). Irradiated by a strong optical beam burns in presence of oxygen. The band structure of ZnTe is shown in Fig.1.19b. In ZnTe hexagonal crystal structure, it has lattice parameters \(a = 0.427\text{nm}\) and \(c = 0.699\text{nm}\) and bandgap 2.23–2.25 eV [108,109].
Fig 1.19a Crystal Structure ZnTe

Fig 1.19b Band Structure of Zinc telluride
1.15.2 Applications of zinc telluride

Zinc telluride can be easily doped and for this reason it is one of the more common semiconducting materials used in optoelectronics. ZnTe is important for development of various semiconductor devices, including blue LEDs, laser diodes, solar cells and components of microwave generators. It can be used for solar cells such as back-surface field layer and p-type semiconductor material for a CdTe/ZnTe structure or in PIN diode structures. The material can also be used as a component of ternary semiconductor compounds, such as CdₙZn₁₋ₙTe which can be made with a varying composition x to allow the optical bandgap to be tuned as desired.

Zinc telluride together with lithium niobate is often used for generation of pulsed terahertz radiation in time-domain terahertz spectroscopy and terahertz imaging. When a crystal of such material is subjected to a high-intensity light pulse of subpicosecond duration, it emits a pulse of terahertz frequency through a nonlinear optical process called optical rectification. Vanadium-doped zinc telluride, ZnTe:V, is a non-linear optical photorefractive material of possible use in the protection of sensors at visible wavelengths.

ZnTe:V optical limiters are light and compact without complicated optics of conventional limiters. ZnTe:V can block a high-intensity jamming beam from a laser dazzler while still passing the lower-intensity image of the observed scene. It can also be used in holographic interferometry, in reconfigurable optical interconnections and in laser optical phase conjugation devices. It offers superior photorefractive
performance at wavelengths between 600–1300 nm, in comparison with other III-V and II-VI compound semiconductors. By adding manganese as an additional dopant (ZnTe:V:Mn), its photorefractive yield can be significantly increased [110].
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