

# Chapter 1

## Semiconductor Materials

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### 1.0 Introduction

In this Chapter, the discussion of semiconductor types and materials used for fabrication of integrated circuit will be presented. The characteristics and properties and their usage are discussed in details.

Semiconductor devices are fabricated using specific materials has the desired physical properties. Semiconductor materials have their conductivity fall in between the conductivity of insulator and conductor. Their conductivity is affected by several factors such as temperature, the incidence of light, the application of a magnetic field and impurities. This versatility makes semiconductor materials very important in electronics and optoelectronics applications.

Semiconductor materials can be classified into many types. They are elemental semiconductor, compound semiconductor, narrow band-gap semiconductor, wide band-gap semiconductor, oxide semiconductor, magnetic semiconductor, polysilicon semiconductor, amorphous semiconductor, organic semiconductor, low dimension semiconductor, and etc. We shall discuss the a few of them.

### 1.1 Elemental Semiconductor

Silicon Si, germanium Ge, and diamond C are important group IV elemental semiconductors. These group IV elemental materials all of them have diamond crystal structure. Another group IV elemental semiconductor having such a structure is alpha tin  $\alpha$ -Sn, which is also referred as gray Sn. Other elemental structures differing from diamond structure include group III element boron (Rhombohedral), group V material phosphorus, and group VI materials such as sulphur S, selenium Se, and tellurium Te.

Currently silicon is the most important semiconductor material used in electronic devices. Some of the important advantages of silicon Si over other semiconductors are:

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- A relative ease of passivating the surface by oxidizing in a controlled manner forming a layer of stable native oxide that substantially reduces the surface recombination velocity.
- Its hardness that large wafers to be handled safely without damaging it.
- It is thermally stable up to 1100<sup>0</sup>C that allows high-temperature processes like diffusion, oxidation, and annealing.
- It is relatively low cost due to established processes.

The basic limitations of silicon are the magnitude and type of its energy band-gap. Its energy band-gap is 1.12eV. It is a direct semiconductor that limits the application in optoelectronics, and it has relatively low carrier mobility as compared to other semiconductor such as gallium arsenide GaAs.

Emerging materials based on Si nanostructures e.g., Si nanocrystals, quantum wires and dots, and porous Si, and Si<sub>1-x</sub>Ge<sub>x</sub> layers grown on Si substrate, appear to be promising materials in various applications. In nanostructures because of quantum confinement of carriers, it leads to increase of electron hole wave function overlap and hence, it increases photon emission efficiency. There is a high energy shift toward the emission blue peak.

Porous Si can be obtained from the anodic etching of crystalline silicon in aqueous hydrofluoric acid HF. It contains a network of pores and crystallites (microscopic crystal) with sizes in the order of several nanometers. This material exhibits relatively efficient luminescence, which is several orders of magnitude higher than that in crystalline Si, and it is believed to be related to the quantum confinement effects in nanocrystalline Si.

In principle, many semiconductors can be grown on Si substrates. For example, the growth of III-V compounds on silicon substrate is attractive since such heterostructures would enable to integrate optical devices in the III-V compound with silicon circuitry on a monolithic chip. III-V compound semiconductors offer a wide range of applications in optoelectronic devices, whereas silicon offers both a convenient electronic device technology and a large area substrate that is mechanically stronger than, III-V compound like GaAs and also has a larger thermal conductivity. The issues related to how to obtain high quality epitaxial heterostructures like GaAs/Si are: the presence of high dislocation densities due to the lattice constant mismatch between the epitaxial layer and substrate; residual stresses in the epitaxial layers due to the difference in thermal expansion coefficients of the epitaxial layer and substrate, and the formation of structural defects like antiphase boundaries due to the epitaxial growth of a polar crystal in the case of GaAs on a nonpolar substrate

like silicon Various approaches are being used to overcome these problems. These include thermal cycle annealing, growth interrupts, selective area growth, and insertion of strained-layer superlattices.

### 1.2 Compound Semiconductor

There are many compound semiconductor materials. They are usually formed from III-V group, II-VI, IV-VI, I-III-VI<sub>2</sub> elements. III-V group semiconductors are GaAs, GaP, GaN, AlAs, InSb, InAs, InP etc. In general, these crystallized materials have relatively high degree of stoichiometry (chemistry deal with the relative quantities of reactants and products in chemical reactions). Many of these compounds such as GaAs, InAs, InP, and indium antimonide InSb have direct energy band-gaps and high carrier mobilities. Thus, the common applications of these semiconductors are used to design a variety of optoelectronic devices for both the detection and generation of electromagnetic radiation, and also in high-speed electronic devices. The energy band-gaps of these compounds are useful for optoelectronic applications. The energy band-gap ranges from 0.17eV for InSb to 3.44eV for GaN covering the wavelength range from about 7.29 to 0.36 $\mu$ m, which is from infrared through visible and to ultraviolet spectral ranges. Materials such as GaAs and InP are also extensively used as substrates for a wide variety of electronic and optoelectronic devices such as light-emitting devices.

#### 1.2.1 II-VI compound semiconductor

II-VI compound semiconductor such as Zn and Cd-chalcogenides such as compounds with oxygen O, S, Se, and tellurium Te cover a wide range of electronic and optical properties due to the wide variations in their energy band-gap. These compounds are also relatively easily miscible (can be mixed well in any proportion), which allows a continuous “engineering” of various properties. However, the preparation of high-quality materials and the processing technologies are not sufficiently developed in comparison with those related to silicon Si and some III-V compounds. The II-VI compounds are typically *n*-type as grown, except ZnTe, which is *p*-type. Among these compounds, the conductivity type of CdTe can be changed by doping, and thus *n*- and *p*-type materials can be obtained. Others II-VI compound such as ZnSe, ZnS and CdS can be doped to produce a small majority of holes. For device applications, it is possible to form heterojunctions in which the *n*- and *p*-sides of the junction are of different II-VI compound semiconductors, and to use metal-semiconductor and metal-insulator-semiconductor structures for carrier-injection device applications. All the II-VI compound semiconductors have direct energy band-

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gaps, thus, high efficient emission or absorption of electromagnetic radiation can be expected from these materials. Therefore, these semiconductors are important mainly for their optical properties. In addition to the binary II-VI compounds, materials such as ternary compound like  $Zn_{1-x}Cd_xS$  and  $ZnS_xSe_{1-x}$ , and quaternary compound such as  $Zn_{1-x}Cd_xS_ySe_{1-y}$  alloys with “engineered” properties are also of interest.

### 1.2.2 IV-VI Compound Semiconductor

IV-VI compound semiconductor like lead chalcogenides such as PbS, PbSe, and PbTe are characterized by narrow energy gaps, high carrier mobilities, and high dielectric constants. The unique feature of the direct energy gap in these compounds is that its energy band-gap increases with increasing temperature, which means the energy gap has a positive temperature coefficient, PTC. In contrast to the temperature behavior of the energy band-gap in other elemental and compound semiconductors, they have a negative temperature coefficient. Main applications of these compounds are in light emitting devices and detectors in the infrared spectral region.

### 1.2.2 I-III-VI<sub>2</sub> Chalcopyrite Compound Semiconductor

I-III-VI<sub>2</sub> chalcopyrite compound semiconductor such as CuAlS<sub>2</sub>, CuGaS<sub>2</sub>, and CuInSe<sub>2</sub> are direct semiconductors that have energy band-gaps between 1.0eV to 3.5eV. In additional CuAlS<sub>2</sub>, CuGaS<sub>2</sub> can be made into *p*-type which is suitable for making heterojunction with wide energy band-gap *n*-type II-VI compound semiconductor. Some possible applications of this compound semiconductor are light emitting device and photovoltaic solar cells.

### 1.2.3 Layer Compound Semiconductor

Layered compounds are examples of a specific covalent van der Waals structure. The compounds that have attracted interest in various applications are layered transition metal dichalcogenides, such as MoS<sub>2</sub>, and ZrS<sub>2</sub> with energy gaps of about 2.0eV, compounds such as HgI<sub>2</sub> and PbI<sub>2</sub> with energy gaps of about 2.1 and 2.3 eV, respectively, and GaSe and InSe with the energy band-gaps of about 2 and 1.2 eV, respectively. In these materials, the bonding is covalent within the layers, which are held together by the weak van der Waals bonding. The fact that layered compounds are strongly bound in two directions by the covalent bonding and weakly bound in the third direction i.e. *c*-axis leads to anisotropy of the structural and physical properties of these semiconductors.

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These compounds are essentially quasi-two-dimensional systems. Thus, some physical properties in such structures may exhibit a two-dimensional behavior.

Since only weak van der Waals forces act between the layers of these compounds, it is possible to introduce a variety of foreign atoms and some organic molecules between the layers forming the intercalation compounds. Such an intercalation process has been extensively demonstrated in layered transition metal dichalcogenides. These intercalation compounds exhibit significant changes in a wide variety of properties as compared to the nonintercalated materials. The process of intercalation is reversible, and thus such layered compounds may be used, e.g., as cathodes in rechargeable high-energy-density batteries, in which the cell reaction is the reversible intercalation of the layered crystals.

The presence of weak van der Waals bonds between the layers also accounts for easy cleavage, implying somewhat delicate handling of bulk materials in various device applications. For example, one of the problems related to applications of such promising semiconductors as  $\text{HgI}_2$  and  $\text{PbI}_2$  in nuclear detectors is the fact that their layered crystal structure makes these materials soft and fragile.

### 1.3 Narrow Band-gap Semiconductor

Narrow band-gap semiconductors such as InSb, InAs, PbSe, PbTe, and PbS have the energy band-gap below about 0.5eV and they are direct semiconductor materials. These semiconductor materials are extensively employed in such infrared optoelectronic device applications as detectors and diode lasers.

Photoconductive lead sulphide PbS and lead selenide PbSe detectors can be employed in the spectral range between about 1.0 and 6.0 $\mu\text{m}$ . Another important material used as a detector in the infrared range is  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ .  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  epitaxial layer can be grown on cadmium telluride CdTe substrate, lattice-matched with  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  substrate or CdTeSe substrate. The energy band-gap of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  between 0 to 1.56eV depending of x value. In addition to these semiconductors, superlattice structures and QWs can also be employed in infrared detector applications. For example, HgTe-CdTe superlattices may offer substantially less tunneling noise as compared to  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  and better control cut-off wavelength over material having the same energy.

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### 1.4 Wide Band-gap Semiconductor

Wide band-gap semiconductor is also referred as refractory semiconductors since they are employed in high temperature application. The typical types of this semiconductor are SiC and II-V nitrides that have high thermal conductivity, high saturation electron drift velocity, high breakdown electric field, and superior chemical and physical stability. The semiconductor has high thermal conductivity indicates it can be used in high temperature at high power level operation. It has wide band-gap that enables detection and emission of light in short-wavelength region likes blue and ultraviolet. It has high saturation electron drift velocity that can be used in RF and microwave operations. High breakdown electric field enables the realization of high power electronic devices and also allows high device packing density for integrated circuit.

Some major present applications of some wide energy-gap semiconductors are in the design of short-wavelength light emitters and detectors optoelectronic devices operating in the blue, violet and ultraviolet spectral regions as well as in high-temperature and high-power devices. A short-wavelength blue laser would substantially increase the storage density for optical recording, as compared to the devices operating at longer wavelengths in between the red and the near infrared. With the use of wide energy-gap semiconductors it also becomes feasible to produce full-color flat-panel displays.

### 1.5 Oxide Semiconductor

Oxide semiconductors are also referred as semiconductor ceramics. These materials are polycrystalline and polyphase materials with grain sizes in the range between 1.0 to 10.0 $\mu\text{m}$ . The properties of grains and grain boundaries play a crucial role in both the understanding and application of the materials. It has been established that (i) the grain boundaries generally have an associated space charge region controlled by the defect structure of the material, (ii) the grain boundaries are paths for the rapid diffusion for various impurities, and (iii) grain boundary segregation, precipitation, and oxidation typically affect various properties of these materials.

Some examples of oxide semiconductors are  $\text{Cu}_2\text{O}$  with energy band-gap of 2.1eV,  $\text{Bi}_2\text{O}_3$  with energy band-gap of 2.8eV,  $\text{ZnO}$  of energy band-gap of 3.4eV,  $\text{LiNbO}_3$  of energy band-gap of 4.0eV etc. They are used in electronic devices and sensors such as positive temperature coefficient PTC thermistor, varistor - resistor with non-linear but symmetric current-voltage characteristics, capacitor of high dielectric constant, gas sensor, and electro-optic modulators.

### 1.6 Magnetic Semiconductor

Semiconductor compound that contains magnetic ions such as Cr, Mn, Fe, Co, Ni, and europium Eu may exhibit magnetic properties. Some oxides such as FeO and NiO exhibit antiferromagnetic properties and oxide such as europium oxide EuO and EuS are ferromagnetic properties. The semiconductor exhibits large magneto-optical effect that can be used to design optical modulators.

### 1.7 Organic Semiconductor

The main advantages of organic semiconductors include their diversity and relative ease of changing their properties to specific applications. Some examples of organic semiconductors include materials such as anthracene  $\text{CH}_{14}\text{H}_{10}$  and polyacetylene  $(\text{CH})_n$ . The electrical conductivity of polyacetylene can be varied by many orders of magnitude by doping with donors such as alkali metals or acceptors such as iodine or  $\text{AsF}_4$ . In the early experiments, it has demonstrated that anthracene and others are photoconductors. Indeed, the first practical application with anthracene was used as photoreceptor material in imaging systems, which is electrophotography. Currently, various organic photoreceptors are widely employed in these applications, offering low cost and relative ease of preparation in flexible configurations.

Typically, these materials exhibit carrier trapping and low mobility, which limit their applications in electronic devices. However, some important applications of organic semiconductors with conjugated bonds are emerging in various electronic and photonic applications, such as transistors, LEDs, solar cells, and nonlinear optical materials, whereby along the chain, a conjugated polymer has alternating single and double bonds between the carbons, which is has  $-\text{C} = \text{C}-\text{C} = \text{C}-$  structural chain.

One of the promising applications of organic semiconductors is in less expensive light emitting diode, covering whole the spectrum of colors, including blue color. The main advantages of organic materials in such applications include low operating voltages, color tunability, and relative simplicity of device fabrication. The actual device incorporates an organic semiconductor - a light emitting layer, sandwiched between two electrodes having dissimilar work functions. In such a case, light emission results from the recombination of electrons injected from a lower work function electrode with holes injected from a higher work function electrode into the organic layer resulting double injections into the light emitting organic semiconductor. Important issues of concern in such applications are the device stability and the

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operational lifetime of organic LED. These issues have something to do with the control of metal and the polymer interface.

Some other applications of organic semiconductors are realized in combination with inorganic semiconductors in hybrid inorganic-organic devices such as nanocrystal based quantum dot-organic systems. For an example, poly *p*-phenylene vinylene PPV, which has the energy band-gap approximately 3.0eV, has been used in combination with cadmium selenide CdSe nanocrystals to make electroluminescent device structure. In this case, the luminescence is due to the recombination of holes injected into a PPV layer with electrons injected into a multilayer film of CdSe nanocrystals. The luminescence spectrum is in the visible spectral region. The system can be adjusted by changing the nanocrystal size.

Although the inadequate stability of organic semiconductors may hinder some of their applications but their high reactivity accompanied by variations in conductivity also implies that a possible application of organic semiconductors in various sensor instruments such as gas sensors and biosensors.

### 1.8 Polycrystalline Semiconductor

Grain boundaries play a crucial role in determining the properties of polycrystalline semiconductors. These semiconductors can be further classified as follows:

- Microcrystalline and nanocrystalline materials that are usually prepared as thin films.
- Large grain materials in the form of sliced ingots and sheets.

The grain size in polycrystalline materials depends on the substrate temperature during thin film growth, the thickness of the film, and also on post-growth annealing treatment of the film. The grain boundaries generally have an associated space charge region controlled by the defect structure of the material, and the grain boundaries are paths for the rapid diffusion of impurities affecting various properties of polycrystalline materials. An important consequence of the presence of potential barriers on grain boundaries in a polycrystalline semiconductor is the increase of its electrical resistivity. One of the important processes is the decoration of grain boundaries, i.e., the process in which precipitates of impurity elements segregate to the boundaries.

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In general, the grain boundaries introduce allowed levels in the energy gap of a semiconductor and act as efficient recombination centers for the minority carriers. This effect is important in minority-carrier devices, such as photovoltaic solar cells and it is expected that some of the photogenerated carriers to be lost through recombination on the grain boundaries. Typically, the efficiency of the device will improve with increasing grain size. In this context, the *columnar grain* structure, which is the grains in a polycrystalline material extends across the wafer thickness, is more desirable as compared to the material containing fine grains that do not extend from back to front of a device structure. In order to prevent significant grain-boundary recombination of the minority carriers, it is also desirable that the lateral grain sizes in the material be larger than the minority carrier diffusion length. It should also be mentioned that the possible preferential diffusion of dopants along the grain boundaries and/or precipitates of impurity elements segregated at the boundaries may provide shunting or conducting paths for current flow across the device junction.

It should be noted that the hydrogen passivation of grain boundaries in polycrystalline silicon devices such as photovoltaic cells is an effective method of improving their photovoltaic performance efficiency. This improvement is associated with the mechanism similar to that of the passivation of dangling bonds in amorphous silicon. It should be added that the hydrogen passivation of other defects, such as dangling bonds at vacancies and dislocations, is also beneficial in improving the performance of photovoltaic cell.

### 1.9 Amorphous Semiconductor

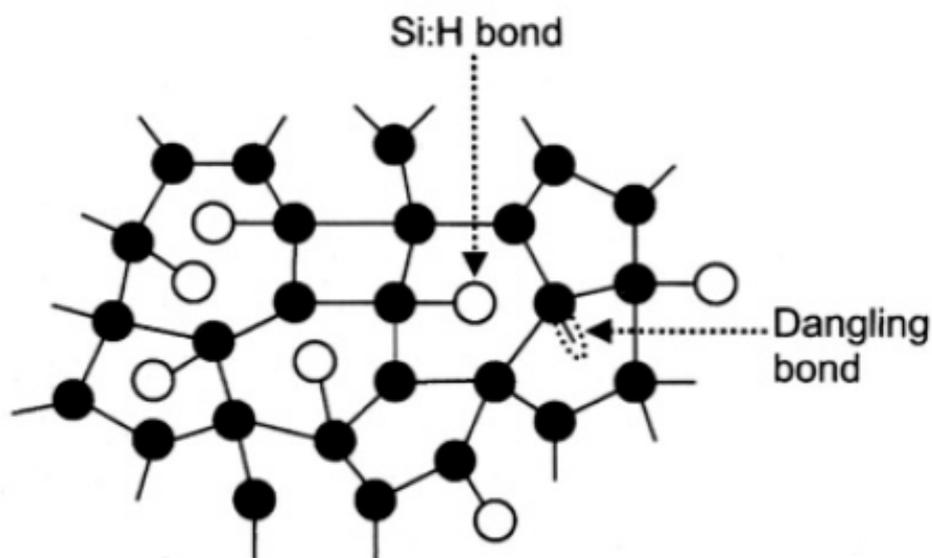
Amorphous semiconductors have found a wide range of applications in various devices. These materials can be relatively inexpensively produced as thin films deposited on large area substrates. Some common examples include the use of amorphous selenium as a photoreceptor material in electrophotographic copiers and of hydrogenated amorphous silicon in solar cells and flat-panel displays.

Some of the important amorphous semiconductors include *amorphous chalcogenides* such as *a*-Se and *a*-As<sub>2</sub>Se<sub>3</sub> and *tetrahedrally-bonded amorphous semiconductors* such as *a*-Si:H).

Amorphous semiconductors have only short range order with no periodic structure as shown in Fig. 1.1. In such cases, some information about the structure such as about the atomic array or atomic distribution, can be obtained by plotting the *radial distribution function*, which is the probability  $P(r)$  of finding an atom at a distance  $r$  from a given atom. In crystalline solids such a

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radial distribution function exhibits series of sharp peaks indicative of the long range order. The curve representing an amorphous material indicates the presence of the short range order only. This also implies that the number of nearest neighbors to any given atom on average is not much different from the corresponding number in the crystalline material. In amorphous materials, there are certain bond length and bond angle variations but on average the density is similar to that corresponding to the crystalline material. In amorphous semiconductors, defects are mainly related to the deviations from the average coordination number, bond length, and bond angle. Other defects include dangling bonds, deviations from an optimal bonding arrangement, and microvoids.



**Figure 1.1:** Random bond structure of amorphous silicon

The electronic band structure of amorphous semiconductors is substantially different from that in the crystalline semiconductors as shown in Fig. 1.2. In crystalline materials, the periodicity of the atomic structure and the presence of long range order result in a band structure with allowed and forbidden electronic levels, with sharp band edges and a fundamental energy band-gap separating valence band from the conduction band. In amorphous semiconductors, there is still a fundamental energy band-gap based on the short range bonding between the atoms. However, the sharp band edges of the crystalline semiconductor are replaced in the amorphous material by *exponential band tails* due to localized states related to the structural disorder, which is due to bond length and bond angle deviations that broaden the distribution of electronic states. In addition, defects like dangling bonds introduce electronic levels in the energy band-gap. It should be noted that the transition from the localized states to the extended states results in a sharp change in the carrier mobility leading to the presence of the mobility edges for corresponding conduction and valence bands or the

mobility gap. The carrier mobility in the extended states is higher and the transport process is analogous to that in crystalline materials, whereas in the localized states, the mobility is due to thermally activated tunneling between the localized states, which is *hopping conduction* and it is lower as compared to the extended states.

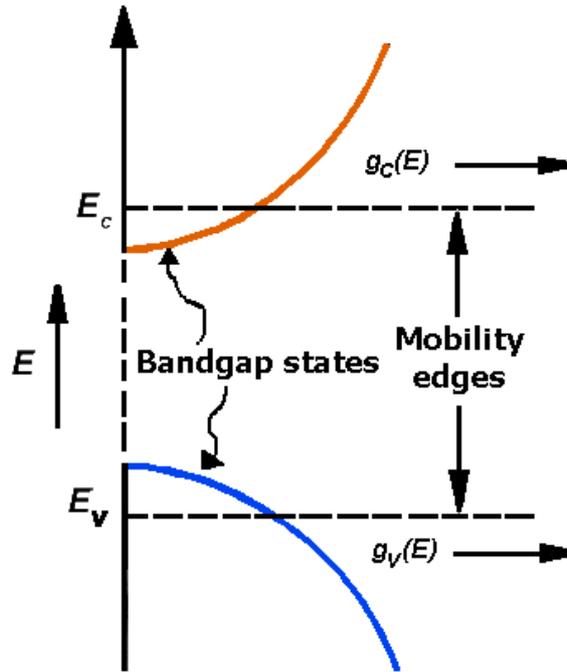


Figure 1.2: Energy band diagram of amorphous silicon

As mentioned, in amorphous semiconductors, the allowed energy bands have band tails in the energy band-gap. The typically observed exponential energy dependence of the absorption edge or exponential absorption edge, which is the *Urbach edge*, provides an important parameter for characterizing the material's quality and it usually depends on the deposition method and deposition conditions. Several models have been proposed to explain this widely observed behavior. In amorphous semiconductors, the shape of the absorption edge can be explained in terms of the joint density of states DOS of the valence and conduction band tails.

An important consequence of the long range disorder in amorphous semiconductors is that one can no longer use the periodic potential  $V(r)$  and derive  $E(k)$  relationship. The energy bands in this case are described by a DOS distribution  $N(E)$ . Since momentum conservation rules or direct and indirect optical transitions no longer apply to case of amorphous silicon. Thus, it has very high absorption coefficient allowing the use of only micrometer scale thin film for absorption of solar energy.

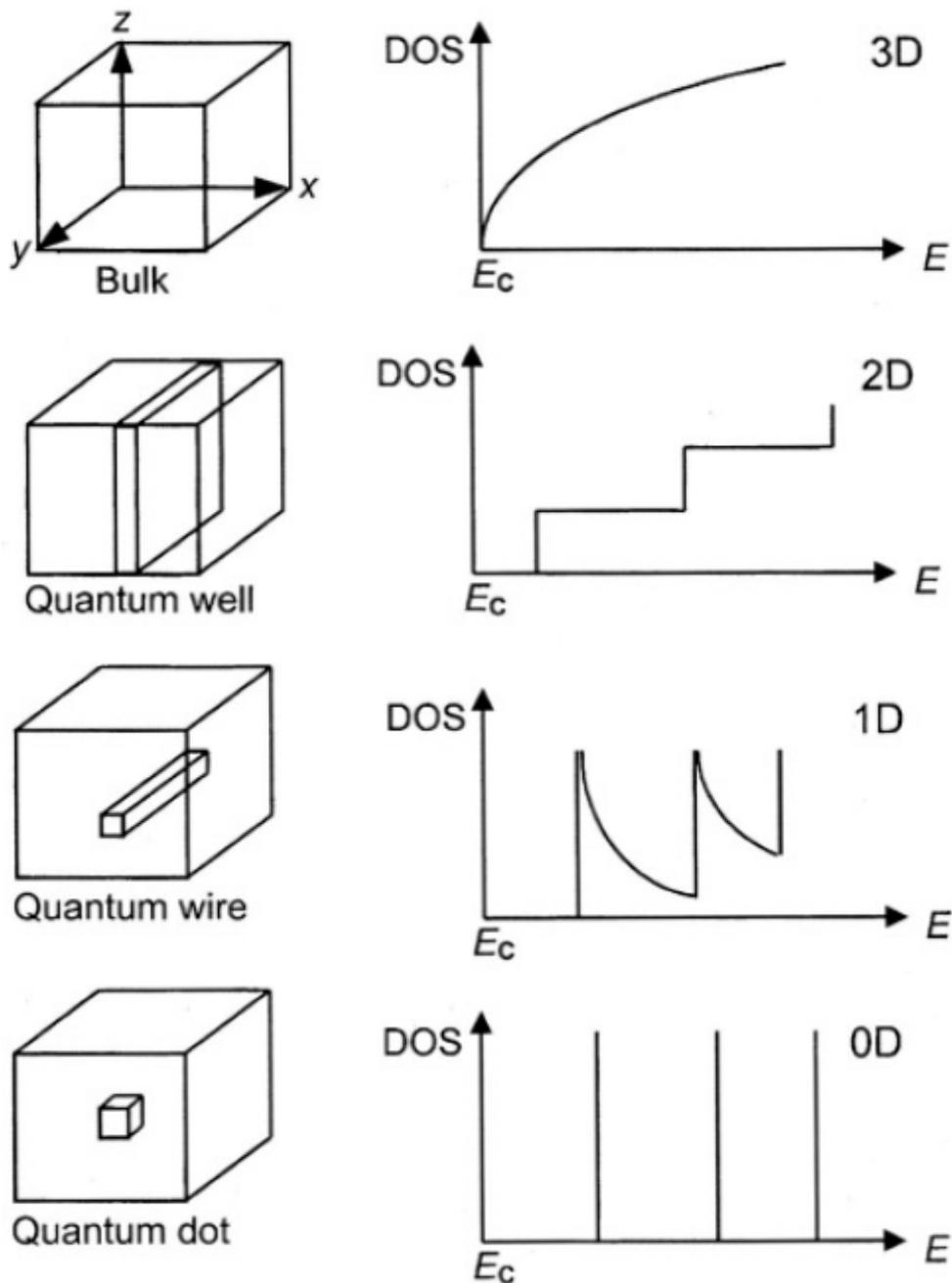
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### 1.10 Low Dimensional Semiconductor

Recent developments related to nanoengineered materials have demonstrated that the nanostructured semiconductors offer increasingly greater flexibility and control in designing various nanoscale structures and devices. In this context, the main motivation is related to continuous trends towards increasing miniaturization of various structures and devices, improving dimensional precision, and controlling and designing various materials properties. One of the important features of nanostructures with typical sizes in the range between about 1 and 50 nm is the flexibility of controlling and designing the properties of such materials by controlling the sizes of nanostructures. Such nanostructures exhibit structural, optical, and electronic properties that are unique to them and that are different from both macroscopic materials and isolated molecules.

Nanostructures have dimensions in the range between about 1 and 50 nm. In this range, the properties of semiconductors are modified and correspond to those that are characteristic of the quantum mechanical electronic confinement, and they exhibit fundamentally different properties as compared to the bulk structures. The characterization of such nanoscale structures can be accomplished by using various scanning probe microscopies SPM, as well as electron microscopy techniques and optical spectroscopy methods.

In nanoscale structures with the dimensions commensurate with the de Broglie wavelength of the charge carriers, the electronic energy levels exhibit quantum confinement effects. Low dimensional structures as shown in Fig. 1.3 include QWs, where the charge carrier motion is allowed in two dimensions only (referred to as one-dimensional confinement), *quantum wires* where the charge carrier motion is allowed in one dimension only (referred to as two-dimensional confinement), and *quantum dots* QDs, where the charge carrier motion is allowed in zero dimensions (referred to as three-dimensional confinement). For these low-dimensional structures as shown in Fig. 1.3 their corresponding DOS as a function of energy. It should be noted that electrons propagating in the QW are also referred to as a *two-dimensional electron gas*, and those propagating in the quantum wire are called a *one-dimensional electron gas*.



**Figure 1.3:** Schematics showing the low dimensional structures and their DOS as the function of energy

## Exercises

- 1.1. Name two factors that make silicon the most attractive semiconductor material in electronic application.
- 1.2. Name three properties and applications of wide band-gap semiconductor materials.

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### Bibliography

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2. Sheila Prasad, Hermann Schumacher, and Anand Gopinath, “*High-Speed Electronics and Optoelectronics: Devices and Circuits*”, Cambridge University Press, 2009.

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#### 2

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#### A

Alpha tin..... *See* Semiconductor

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Organic semiconductor..... 1, 6

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Polysilicon semiconductor .....	1

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Quantum wire.....	11

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Cadmium telluride .....	4

Gallium nitride .....	3
Hg <sub>1-x</sub> Cd <sub>x</sub> Te .....	4
Indium arsenide .....	4
Lead selenide .....	4
Lead sulphide .....	4
Lead telluride.....	4
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Wide band-gap semiconductor .....	1, 5
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