Unit 25

Solids

This unit online, with its interactives:
science-playground.com/s/11f25

Copper carries electricity a hundred billion times better than pure silicon, and glass about a hundred billion billion times worse. Yet the three are made of atoms with much the same parts: a nucleus and electrons. Why should one solid let electrons flow and another hold them still?

The answer starts inside a single atom, whose electrons can only have certain energies, like the rungs of a ladder. Pack billions of atoms into a solid and the rungs crowd together into broad **bands**, separated by gaps no electron can stand in. How full the top bands are, and how wide the gap above them, decides whether a solid is a conductor, an insulator or a semiconductor. Semiconductors, with a small gap, can be changed at will, by warming them, shining light on them or adding a few atoms of another element. That is the trick behind every phone, solar panel and LED.

25.1 Energy levels

In the nuclear model of the atom (Unit 24), the electrons around a nucleus can't have just any energy. Each electron is limited to certain **energy levels**, and an electron can change its energy only by jumping from one allowed level to another. Why only these levels are allowed takes the wave nature of the electron and quantum mechanics to explain (see Bohr's staircase in Going Further). For now, accept that this is how nature works.

The levels can be drawn as horizontal lines one above the other, like a ladder with unequally spaced rungs, each line at the height of its energy: an **energy level diagram**. Every kind of atom has its own set of levels. An electron can move from one level to another by gaining or losing exactly the difference in energy, but it can never have an energy between two levels. So an atom can only take in or give out energy in parcels of certain definite sizes: its energy is **quantized**.

Hydrogen is the simplest atom: one proton with one electron bound to it by the electric force. If the atom loses its electron completely, it becomes a positive hydrogen ion. A common picture of the atom is the "planetary model", with the electron going

round the proton like the Earth round the Sun. It has weaknesses (an electron doesn't follow a path), but it is a good introduction to energy levels.

The energy levels of the hydrogen atom are:

Energy level, n	Energy (eV)
1	-13.6
2	-3.40
3	-1.51
4	-0.85
5	-0.54
∞	0

They follow one rule, $E_n = -\dfrac{13.6\ \text{eV}}{n^2}$: level 2 is $-13.6/4 = -3.40$ eV, level 3 is $-13.6/9 = -1.51$ eV.

Energies are negative because the zero is chosen with the electron free and at rest, far from the proton; a bound electron has less energy than that. An electron in the **ground state** of hydrogen, level 1, has exactly -13.6 eV, so 13.6 eV is needed to free it: hydrogen's **ionization energy**. An atom with an electron in a level above the ground state is **excited**: an electron in level 2 is in the **first excited state**, one in level 3 in the **second excited state**, and so on.

The levels are **discrete**: an electron in a hydrogen atom can't have -5.92 eV or -10.21 eV, or any other value between -13.6 eV and -3.40 eV. It must have one of the values in the table.

Answer these questions

13. On the basis of the band theory of solids, how would you distinguish between a conductor and a semiconductor?
14. How is a p-type semiconductor formed? Explain.
15. When p-type and n-type materials are joined, a depletion layer forms at the junction. Why?
16. How does the conductivity of a semiconductor vary with temperature? Explain.
17. The conductivity of an intrinsic semiconductor is low. Why?
18. Why is a semiconductor virtually an insulator at room temperature?
19. What do you mean by doping?
20. What do you mean by the forbidden energy gap?
21. What is an extrinsic semiconductor? Explain the formation of the potential barrier and the depletion layer at a p–n junction.

A companion to your textbook, not a replacement for it: study from the book your school uses, and where the two differ, follow your teacher. Found a mistake? Please tell us.

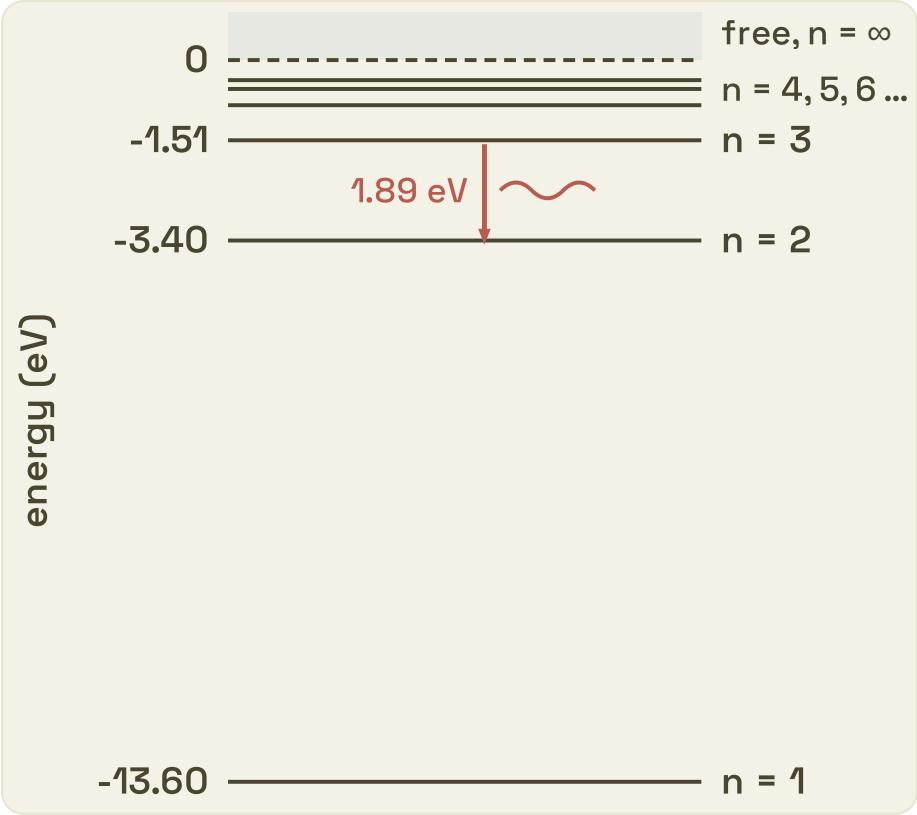


Figure 25.1 *The energy level diagram of hydrogen, to scale. The levels crowd together towards 0 eV, where the electron is no longer bound: the atom is ionized. An electron dropping from level 3 to level 2 gives out a photon of 3.40 − 1.51 = 1.89 eV, the red line of hydrogen's spectrum.*

Check 1

An electron in a hydrogen atom is in the second excited state. How much energy is needed to free it from the atom?

a 13.6 eV
b 3.40 eV
c 1.51 eV
d 0.85 eV

25.2 Band theory

A single atom has sharp, separate energy levels. What happens to them when many atoms are packed together into a solid?

When two identical atoms are far apart, each has the same set of levels. Bring them close, and the electron waves of the two atoms overlap: each level splits into **two** levels, slightly apart. Bring together three atoms and each level becomes three; a grain of silicon has about 10^{20} atoms, so each level becomes 10^{20} levels, so close together that they form a continuous **band** of allowed energies, shared by all the atoms of the solid. Between the bands are **gaps**, ranges of energy where there are no allowed levels at all: the **forbidden bands**.

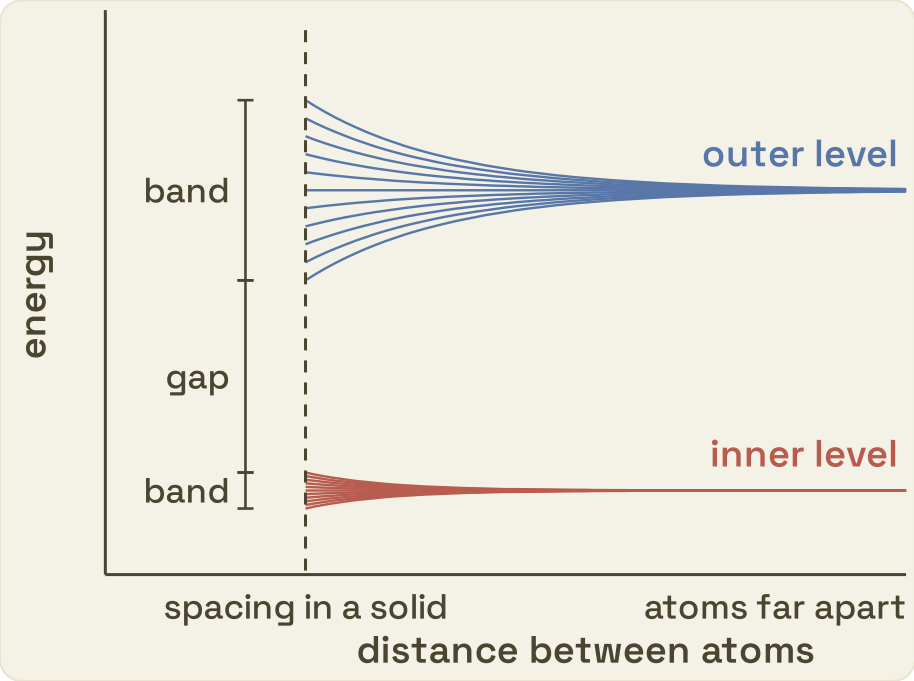


Figure 25.2 *Energy levels as atoms come together. Far apart (right), every atom has the same sharp levels. At the spacing of the atoms in a solid (left), the electron waves overlap and each level spreads into a band of very many levels, with a forbidden gap between the bands. The outer levels, whose electrons reach farthest, spread the most.*

The **valence band** is the highest band that contains electrons at absolute zero; it holds the electrons of the bonds between the atoms. The band above it is the **conduction band**. Electrons in the conduction band are free to move through the solid and carry a current. The gap between the top of the valence band and the bottom of the conduction band is the **forbidden energy gap**, or **band gap**, E_g.

For a current to flow, electrons must be able to gain a little energy from the electric field, which means moving into empty levels just above their own. In a **full** band

Check 10

7. When arsenic is added as an impurity to silicon, the resulting material is:

a an n-type conductor
b an n-type semiconductor
c a p-type conductor
d a p-type semiconductor

Check 11

8. Three semiconductors are arranged in increasing order of their energy gaps. The correct arrangement is:

a tellurium, germanium, silicon
b tellurium, silicon, germanium
c silicon, germanium, tellurium
d silicon, tellurium, germanium

Check 12

9. A p-type semiconductor is:

a a silicon crystal doped with arsenic
b a silicon crystal doped with antimony
c a germanium crystal doped with boron
d a germanium crystal doped with phosphorus

Check 13

10. The current through a p–n junction is negligible when the junction is:

a forward biased
b reverse biased
c positive biased
d negative biased

Check 14

11. Silicon is a semiconductor. On adding a small quantity of arsenic to it, its conductivity:

a increases
b decreases
c remains the same
d becomes zero

Check 15

12. Indium is mixed into a silicon specimen, on average one indium atom per 10^8 silicon atoms. If the number density of atoms in the silicon is 5×10^{28} atoms/m^3, the number and nature of the impurity atoms per cubic meter are:

a 5×10^{20}, acceptor
b 5×10^{20}, donor
c 5×10^{36}, acceptor
d 5×10^{36}, donor

Exercise

Choose the correct option

Check 5

1. The barrier potential difference is the potential difference across:

a the terminals of a cell
b the depletion layer
c capacitor plates
d the ends of a conductor

Check 6

2. A transformer is a device to:

a convert mechanical energy to electrical energy
b convert a.c. to d.c.
c convert d.c. to a.c.
d change the size of an alternating voltage

3. a.c. is converted to d.c. by a:

a transformer
b rectifier
c diode
d triode

Check 7

4. When pure germanium is doped with a trivalent impurity like aluminium, conduction is due to:

a electrons
b holes
c protons
d positrons

Check 8

5. If germanium is doped with a donor impurity, the donor atoms should be:

a tetravalent
b pentavalent
c trivalent
d none of these

Check 9

6. A sample of n-type silicon:

a contains an excess of free electrons, and is therefore negatively charged
b contains an excess of free electrons, and is electrically neutral
c mostly contains trivalent impurities
d contains only tetravalent impurities

there are no empty levels to move into, so its electrons can't carry a current, however many there are.

Conductors. In a metal, the highest band containing electrons is only **partly filled**, or two bands **overlap**. Either way there are plenty of empty levels of slightly higher energy, so when a potential difference is applied, electrons can speed up and gain energy: a current flows easily.

Insulators. In a good insulator, the valence band is **completely full** and the conduction band is **empty**, with a wide band gap between them, typically **5 to 10 eV** (diamond 5.5 eV, glass about 9 eV). At room temperature (300 K) the average kinetic energy of the particles, $\frac{3}{2}kT$, is only about 0.04 eV:

$$\tfrac{3}{2}kT = 1.5 \times (1.38 \times 10^{-23}) \times 300 = 6.2 \times 10^{-21}\ \text{J} = \frac{6.2 \times 10^{-21}}{1.6 \times 10^{-19}}\ \text{eV} = 0.039\ \text{eV}$$

So almost no electron can gain the 5 eV or more needed to cross the gap. When a potential difference is applied, there are no free levels the electrons can reach, and no current flows.

Semiconductors. A pure (or **intrinsic**) semiconductor, such as silicon or germanium, has bands like an insulator's, but its band gap is much smaller, about **1 eV** (silicon 1.12 eV, germanium 0.67 eV at room temperature). At room temperature a few electrons gain enough thermal energy to jump the gap into the conduction band, so a very small current can flow when a voltage is applied. At higher temperatures more electrons can jump the gap, so the resistivity of a semiconductor **decreases** as its temperature rises.

The widget below works these numbers out from the band gap and the temperature.

Holes

That is not all there is to a semiconductor's current. When an electron jumps to the conduction band, it leaves an empty level behind in the valence band. Such an unfilled electron state is called a **hole**.

When a potential difference is applied, the few electrons in the conduction band move towards the positive electrode. The valence electrons are pulled the same way, and a few of them manage to move, by jumping into holes. Each valence electron that fills a hole leaves its own hole behind, one place back. So the holes move the other way, **towards the negative electrode**, as if they were positive charges. A hole carries a charge of $+1.6 \times 10^{-19}$ C, equal and opposite to an electron's.

Electrons gather towards one side of the material and holes towards the other, and **both** carry the current: the electrons in the conduction band, and the holes in the va-

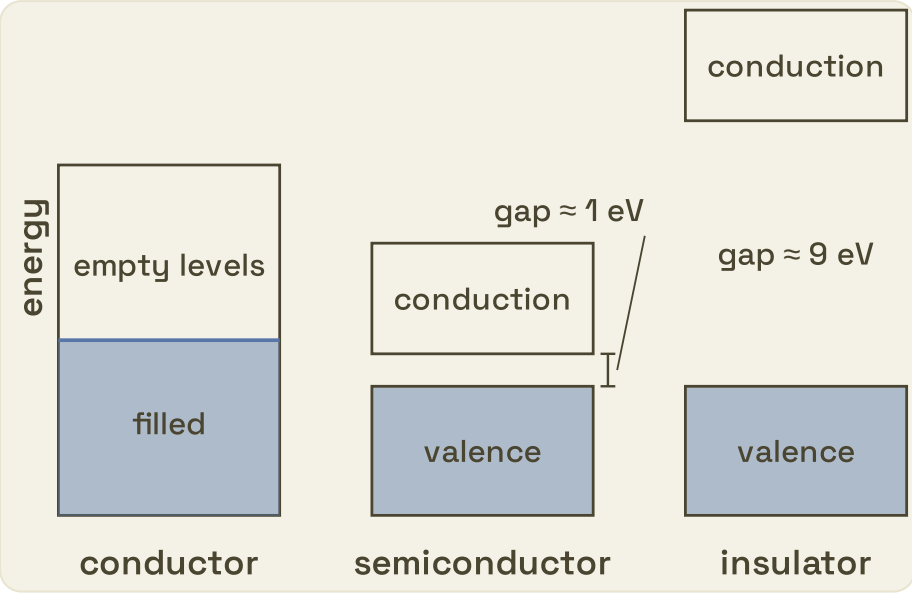


Figure 25.3 *The bands of a conductor, a semiconductor and an insulator, with filled levels shaded. In the conductor the top band is partly filled (or two bands overlap). The semiconductor and the insulator both have a full valence band and an empty conduction band; the semiconductor's gap is small enough for a few electrons to jump it at room temperature.*

CAREFUL

Few, not none

"Only a few electrons can jump the gap" hides a huge number, because the chance of a jump falls off exponentially with the gap. At room temperature, a cubic meter of silicon has about 10^{16} electrons in its conduction band (out of 10^{29} in its bonds), germanium about 2×10^{19}, and diamond fewer than one. Copper has about 8.5×10^{28} free electrons per cubic meter: about one per atom.

lence band.

Points to remember

In an **intrinsic semiconductor at 0 K**:

- the valence band is completely full;
- the conduction band is empty; and
- the forbidden band is about 1 eV wide.

In an **intrinsic semiconductor above 0 K**:

DID YOU KNOW?

Billions of junctions in your pocket

A top phone processor of 2023 holds about 19 billion transistors, each a pattern of p-type and n-type silicon with parts only a few nanometers across, a few tens of silicon atoms. They are made from silicon purified to 99.999 999 999 % (one foreign atom in a hundred billion), then doped on purpose, in tiny measured amounts, exactly where it is wanted.

IN SHORT

Key ideas of Unit 25

- An atom's electrons can only have certain energies, its energy levels; for hydrogen $E_n = -13.6/n^2$ eV: −13.6, −3.40, −1.51, −0.85, −0.54 eV. Level 1 is the ground state; above it, excited states.
- In a solid, each level spreads into a band. The valence band holds the bonding electrons; the conduction band above it, the free ones; between them, the forbidden gap E_g.
- Conductor: top band partly full, or bands overlapping. Insulator: full valence band, empty conduction band, gap 5–10 eV. Semiconductor: like an insulator but with a gap of about 1 eV (Si 1.12, Ge 0.67 eV).
- In a semiconductor, electrons that jump the gap leave holes: positive carriers, moving the opposite way. In a pure one, electrons and holes are equal in number.
- Warming: a semiconductor's resistance falls (many more carriers); a metal's rises (more scattering, no more carriers). Light does the same to an LDR: brighter light, lower resistance.
- Doping: pentavalent donors (P, As, Sb) give free electrons: n-type. Trivalent acceptors (B, Al, Ga, In) give holes: p-type. Majority and minority carriers. Doped crystals are still neutral.
- A p–n junction has a depletion layer and a barrier potential (Si 0.7 V, Ge 0.3 V). Forward biased it conducts; reverse biased, almost not at all: a diode, used in rectifiers to turn a.c. into d.c.

trons trying to cross. Diffusion soon stops. The potential difference across the depletion layer is the **barrier potential**: about **0.7 V** for silicon and 0.3 V for germanium.

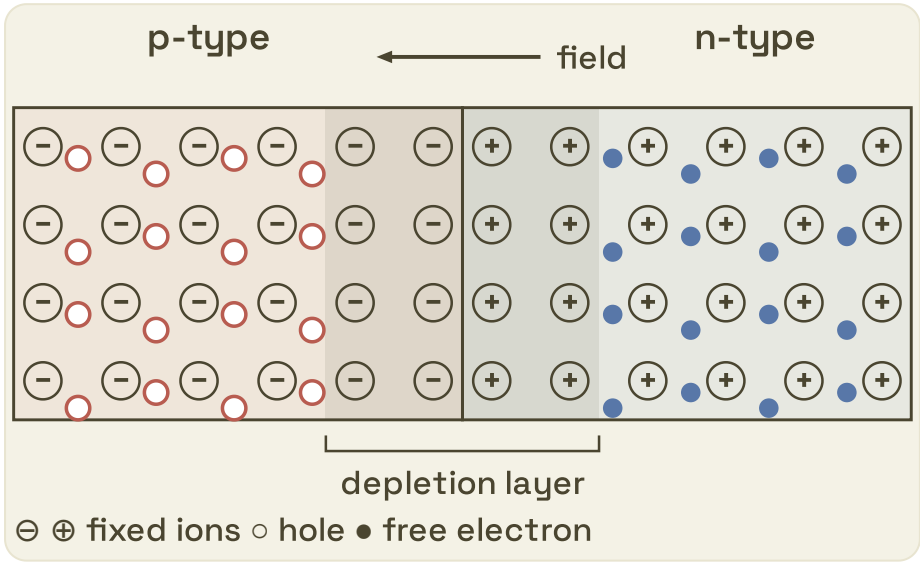


Figure 25.10 *A p–n junction. Free electrons from the n side and holes from the p side have crossed and recombined near the junction, leaving the depletion layer: fixed positive donor ions on the n side and negative acceptor ions on the p side, with no free carriers. Their electric field, from n to p, makes the barrier potential that stops more carriers crossing.*

Bias. A junction with a voltage across it is said to be **biased**.

- **Forward bias**: p side to the positive terminal. The supply's voltage works against the barrier, the depletion layer narrows, and once the supply is above the barrier potential, electrons and holes cross freely: a large current flows.
- **Reverse bias**: p side to the negative terminal. The supply adds to the barrier, the depletion layer widens, and only a tiny current of minority carriers flows, usually less than a microampere.

So a p–n junction, a **diode**, lets current through in one direction only.

Rectifiers and transformers. The mains supply in Nepal is alternating current, 230 V at 50 Hz, but phones, laptops and LEDs need direct current at a few volts. A charger does two jobs. A **transformer** changes the size of an alternating voltage, down from 230 V to a few volts (it works only with a.c.). A **rectifier**, made of diodes, then converts the a.c. to d.c., because each diode passes current only one way: one diode gives half-wave rectification, and four in a bridge use both halves of each wave. A capacitor smooths what is left.

DID YOU KNOW?

The hole is a real particle-like thing

Treating a hole as a positive particle is not just a way of speaking. In the Hall effect (Grade 12), a magnetic field pushes the moving charges in a conductor sideways, and the sign of the voltage it makes shows the sign of the carriers. For metals like copper it shows negative carriers; for some semiconductors, and even for a few metals such as zinc, it shows **positive** carriers: holes.

- some electrons can jump the forbidden band into the conduction band;
- the conduction band's electrons carry current as negative charges;
- the empty states they leave behind in the valence band are called holes;
- holes act as positive charge carriers in the valence band;
- the number of electrons per unit volume in the conduction band (their **number density**) equals the number density of holes in the valence band, since each jump makes one of each;
- the atoms vibrate more as the temperature rises, which on its own would raise the resistance; but the increase in the number of charge carriers far outweighs that, so overall **the resistance decreases as the temperature rises**.

In a **metal**:

- the valence band overlaps the conduction band (or the top band is partly full);
- the number of charge carriers doesn't increase with temperature, because there is no forbidden band to cross;
- the atoms vibrate more as the temperature rises and scatter the electrons more, so **the resistivity increases as the temperature rises**.

In an **insulator**:

- the valence band is full;
- the conduction band is empty;
- the forbidden band is very wide; and
- there are no free electrons (electrons in the conduction band), so it doesn't conduct.

WORKED EXAMPLE

Copper and silicon in hot weather

A copper wire and a piece of pure silicon both warm up from 20 °C to 50 °C. Copper's resistance rises by about 12 %; silicon's falls to about a tenth. Explain the difference.

Answer

In both, the atoms vibrate more strongly at 50 °C, and the moving electrons are scattered more often.

- **Copper** already has about one free electron per atom, and warming it adds no more. The extra scattering is the only change, so its resistance **rises**.
- **Silicon** has very few free carriers, and their number grows steeply with temperature: about ten times more electrons (and holes) jump the 1.12 eV gap at 50 °C than at 20 °C. That increase is far larger than the effect of the extra scattering, so its resistance **falls**.

This is used in a **thermistor**, a semiconductor whose resistance falls sharply as it warms, in thermometers and in circuits that switch on a fan when something gets hot.

Check 2

Why does the resistance of a pure semiconductor decrease as its temperature rises?

a. its atoms vibrate less
b. its band gap becomes zero
c. more electrons gain enough energy to jump the band gap, making more electrons and holes to carry current
d. electrons fall from the conduction band into the valence band

25.3 Light-dependent resistors

Thermal energy is not the only way to lift an electron from the valence band to the conduction band. A photon of light can do it too, if its energy hf is at least the band gap: the same packets of energy that knock electrons out of a metal in the photoelectric effect.

Semiconductor materials can be made with a band gap such that photons of visible light lift electrons into the conduction band. Brighter light means more photons per second, so more electrons lifted to the conduction band (and more holes left behind).

WORKED EXAMPLE

How many acceptor atoms?

A silicon crystal has 5×10^{28} atoms per cubic meter. It is doped with boron, one boron atom for every 10^7 silicon atoms. How many holes per cubic meter does the boron give, and how does this compare with pure silicon's 1×10^{16} holes per cubic meter at room temperature?

Answer

Boron atoms per cubic meter $= \dfrac{5 \times 10^{28}}{10^7} = 5 \times 10^{21}$. Each gives one hole, so the doping gives **5×10^{21} holes per cubic meter**.

$\dfrac{5 \times 10^{21}}{1 \times 10^{16}} = 5 \times 10^5$: half a million times more holes than pure silicon, from one atom in ten million. The holes are the majority carriers by far, and the crystal is p-type.

Check 4

Silicon is doped with gallium. The result is:

a. an n-type semiconductor, with electrons as majority carriers
b. a p-type semiconductor, with holes as majority carriers
c. a p-type semiconductor that is positively charged
d. an intrinsic semiconductor

25.6 The p–n junction

Most uses of semiconductors join p-type and n-type material in one crystal. The boundary between them is a **p–n junction**, and it behaves in a way neither material does alone.

The depletion layer. At the moment the junction forms, the n side has many free electrons and the p side many holes. Free electrons near the junction **diffuse** across it into the p side, and holes into the n side, each spreading from where there are many to where there are few, and they recombine. This leaves a thin layer on each side of the junction, about a micrometer thick, with almost no free carriers: the **depletion layer**. It is not neutral, though: on the n side it holds the positive donor ions the electrons left behind, and on the p side the negative acceptor ions.

The barrier potential. These fixed charges make an electric field across the depletion layer, pointing from the n side to the p side, which pushes back any more elec-

CAREFUL

An n-type semiconductor is not negatively charged

The "n" is for the **carriers**, not the charge. Every free electron in n-type silicon came from a donor atom, which is left as a positive ion, so the crystal as a whole is **neutral**. In the same way, p-type silicon is neutral: each hole is matched by a negative acceptor ion.

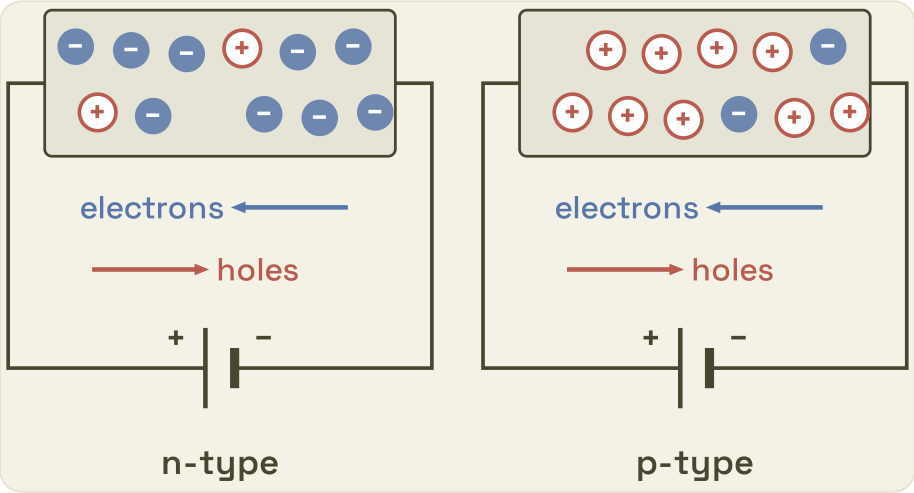


Figure 25.9 *n-type silicon (left) and p-type silicon (right), each joined to a battery with its positive terminal on the left. In both, the free electrons (–) drift to the left, towards the positive terminal, and the holes (+) drift to the right. In n-type the electrons are the many and the holes the few; in p-type the other way round.*

- **In n-type**, the many free electrons reach the left end of the crystal, enter the wire and flow on to the positive terminal of the battery. When one of the few holes reaches the right end, a free electron from the wire there enters the crystal and recombines with it.
- **In p-type**, the many holes reach the right end, where each recombines with a free electron entering from the wire. Meanwhile the few free electrons inside the crystal drift from right to left; because there are so few of these minority carriers, they have almost no effect on the current.

In both, the current in the wires is carried by electrons, and the conventional current flows the same way: out of the battery's positive terminal and round the circuit.

So **the resistance of such a material falls as the intensity of the light increases**. A component made this way is a **light-dependent resistor** (LDR).

The usual material is cadmium sulphide, with a gap of 2.4 eV: photons of wavelength shorter than about 520 nm (green, blue and violet) can lift its electrons. A typical LDR has a resistance of about 1 MΩ in the dark and a few hundred ohms in bright sunlight.

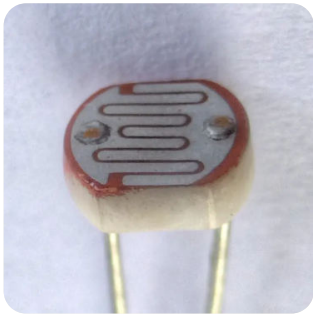


Figure 25.4 *A light-dependent resistor. The wavy track is the cadmium sulphide, between two metal contacts that interlock like fingers, so that a large area of it lies between them.*

Photo: Nevit Dilmen, CC BY-SA 3.0

WORKED EXAMPLE

The longest wavelength an LDR responds to

The band gap of cadmium sulphide is 2.4 eV. Find the longest wavelength of light that can lift an electron across it. ($h = 6.63 \times 10^{-34}$ J s, $c = 3.0 \times 10^{8}$ m/s, $1\ \text{eV} = 1.6 \times 10^{-19}$ J.)

Answer

The photon's energy must be at least the gap: $\dfrac{hc}{\lambda} \geq E_g$, so

$$\lambda_{\max} = \frac{hc}{E_g} = \frac{6.63 \times 10^{-34} \times 3.0 \times 10^{8}}{2.4 \times 1.6 \times 10^{-19}} = 5.2 \times 10^{-7}\ \text{m} = \mathbf{520\ nm}$$

Green light and shorter wavelengths work; red light doesn't. (Silicon's gap, 1.12 eV, gives 1100 nm, in the infrared: that is why silicon solar cells use all visible light, and why phone cameras made of silicon can see a TV remote's infrared flash.)

DID YOU KNOW?

Street lights that switch themselves on

Many street lights and garden lamps in Nepal switch on at dusk by themselves. Inside each is an LDR in a circuit: when the daylight fades, the LDR's resistance rises, the voltage across it rises, and at a set voltage a transistor turns the lamp on. The same idea is in solar garden lights, which charge in the day and glow at night.

25.4 Semiconductors

The best conductors (silver, copper and gold) have **one** electron in their outer shell, easily shared through the whole metal. The best semiconductors, silicon and germanium, have **four**. A **semiconductor** is a material whose electrical properties lie between those of a conductor and those of an insulator. Germanium and silicon are the elements most used; compounds such as gallium arsenide and gallium nitride are semiconductors too.

In a silicon crystal, every atom sits at the center of four neighbors and shares one of its four outer electrons with each. Each pair of shared electrons is a **covalent bond**, so every atom has four bonds and eight shared electrons around it: none is free to move.

The hole

The **ambient temperature** is the temperature of the surroundings. Above absolute zero (−273 °C), the atoms of a silicon crystal vibrate, and the higher the temperature the more strongly they vibrate. (The warmth you feel when you pick up a warm object is the effect of its vibrating atoms.)

Now and then, these vibrations shake an electron out of its bond. It is then free to move through the crystal: in the band picture, it has jumped into the conduction band. Its departure leaves a gap in the bond, a **hole**. The atom it left now has one electron too few, so the hole behaves like a positive charge, and it attracts and captures any free electron that comes near. An electron from a neighboring bond can also slip into it, which moves the hole one bond over.

Holes are the crucial difference between conductors and semiconductors. They let semiconductors do all kinds of things that conductors can't.

At room temperature, thermal energy makes only a few holes and free electrons in silicon: about one bond in 10^{13} is broken. To increase the numbers of holes and free

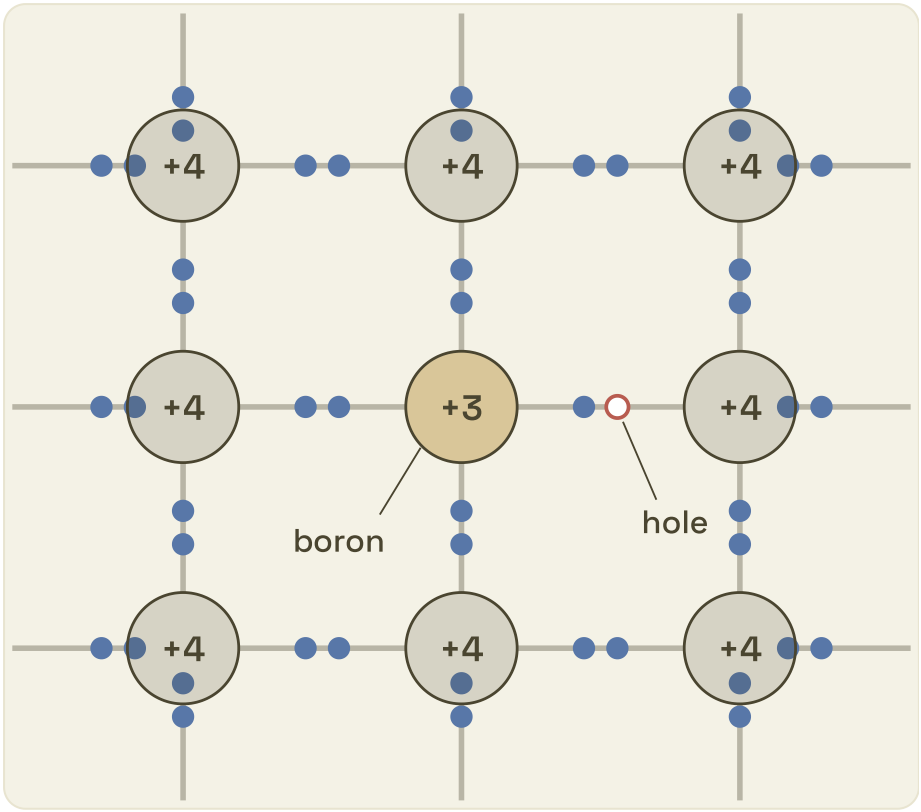


Figure 25.8 *A trivalent atom (here boron, +3) in the silicon crystal. Its three outer electrons form three bonds; the fourth bond is one electron short, a hole, which can accept an electron from a neighboring bond.*

Two types of extrinsic semiconductor

Doping can give a semiconductor either more free electrons than holes, or more holes than free electrons, so doped semiconductors come in two types.

n-type semiconductor. Silicon doped with a pentavalent impurity is an **n-type** semiconductor, n standing for **negative**. The free electrons outnumber the holes, so the free electrons are the **majority carriers** and the holes the **minority carriers**.

p-type semiconductor. Silicon doped with a trivalent impurity is a **p-type** semiconductor, p standing for **positive**. The holes outnumber the free electrons, so the holes are the majority carriers and the free electrons the minority carriers.

In each crystal, the applied voltage moves the free electrons to the left, towards the positive terminal, and the holes to the right.

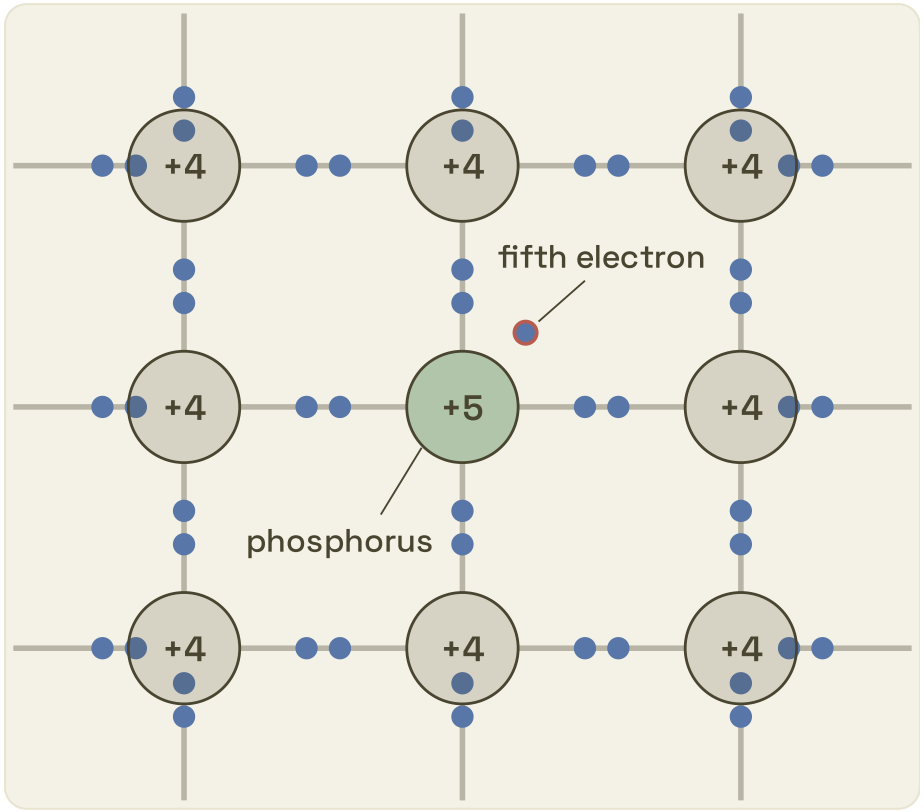


Figure 25.7 *A pentavalent atom (here phosphorus, +5) in the silicon crystal. Four of its five outer electrons form bonds with the four silicon neighbors; the fifth has no bond to join and is only loosely held, so it soon wanders off as a free electron.*

negative ion. A trivalent atom is called an **acceptor** atom because each hole it gives can accept an electron.

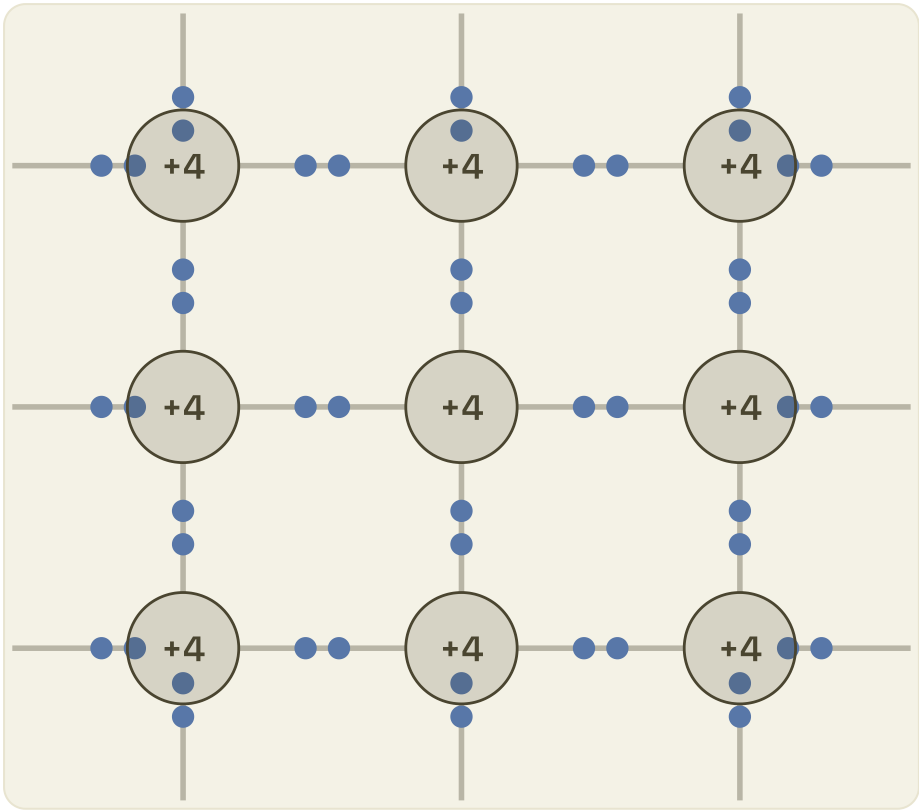


Figure 25.5 *A flat picture of the silicon crystal. Each silicon atom (its core, the nucleus and inner electrons, drawn as a circle marked +4) shares its four outer electrons (dots) with its four neighbors, one pair in each bond. In the real crystal the four neighbors sit at the corners of a tetrahedron round each atom.*

electrons, the crystal is **doped** (section 25.5).

Main ideas

A hole and a free electron each carry a charge of 1.6×10^{-19} C, of opposite signs. At any instant, inside a silicon crystal:

1. heat is **creating** new pairs, a free electron and a hole each;
2. elsewhere, pairs are **recombining**: a free electron falls into a hole, and both disappear;
3. some free electrons and holes exist for a while, waiting to recombine.

The average time between a free electron's creation and its recombination is its **lifetime**: from nanoseconds to milliseconds, depending on the crystal's purity.

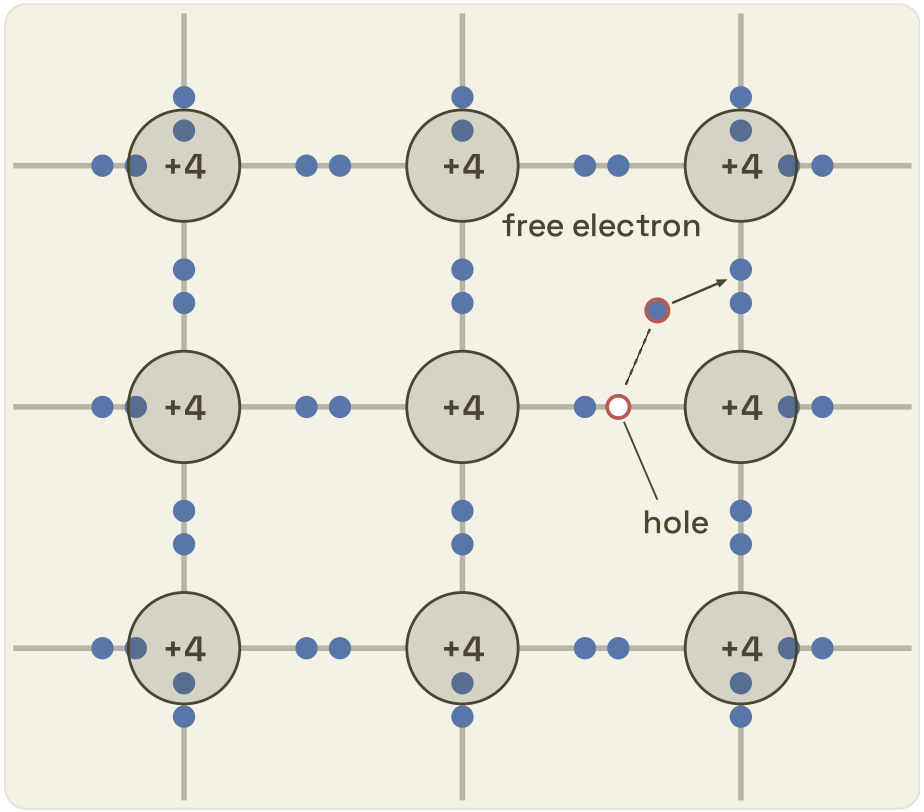


Figure 25.6 *A vibration has shaken an electron free from one bond (it moves off through the crystal) and left a hole in the bond, marked as an empty circle.*

Intrinsic semiconductors

An **intrinsic semiconductor** is a pure one, with no other kind of atom in it: a silicon crystal made of silicon atoms only. At room temperature a silicon crystal is a poor conductor, almost an insulator, because thermal energy makes only a few free electrons and holes.

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In an intrinsic semiconductor, the number of free electrons is:

a much greater than the number of holes

b much less than the number of holes

c equal to the number of holes

d zero at all temperatures

25.5 Doping a semiconductor

To make a semiconductor conduct better, we **dope** it: we add impurity atoms to the pure crystal, on purpose, to change how well it conducts. A doped semiconductor is called an **extrinsic semiconductor**. Only a tiny amount is added, often about one impurity atom per 10^6 to 10^8 silicon atoms, yet it can raise the conductivity of silicon thousands or millions of times.

Increasing the free electrons

How is the impurity put in? One way is to melt pure silicon (at 1414 °C), which breaks the covalent bonds and turns the solid into a liquid, add the impurity, and grow a new crystal from the melt. (Chips are also doped afterwards, by heating the silicon in a gas of the impurity, or firing impurity ions into its surface.)

To increase the number of free electrons, **pentavalent** atoms are added: atoms with five outer (valence) electrons, such as **phosphorus, arsenic and antimony**. They give, or donate, an extra electron to the crystal, so they are called **donor** impurities.

When the doped crystal cools and forms its solid structure again, each pentavalent atom takes a silicon atom's place, surrounded by four silicon atoms. Four of its five outer electrons form bonds with the four neighbors, as a silicon atom's would. The fifth has no bond to join. It is held only very weakly, by about 0.045 eV, so at room temperature, with $\frac{3}{2}kT \approx 0.04$ eV, almost every such electron breaks free and becomes a **free electron**. The donor atom, having lost it, is a fixed positive ion.

So each donor atom in a silicon crystal gives one free electron, and the amount of impurity sets the conductivity: more donors, more free electrons, a better conductor. Silicon with only a little impurity (**lightly** doped) still has a high resistance; silicon with a lot (**heavily** doped) has a low one.

Increasing the number of holes

To make an excess of holes, a **trivalent** impurity is used, one whose atoms have only three valence electrons: **boron, aluminium, gallium** or **indium**.

A trivalent atom in the crystal is surrounded by four silicon atoms. It has only three outer electrons to share, so one of its four bonds is one electron short: there is a hole beside each trivalent atom. An electron from a neighboring bond easily moves into it (this takes only about 0.045 eV for boron), and the hole moves away through the crystal as a free hole, while the boron atom, now with an extra electron, becomes a fixed