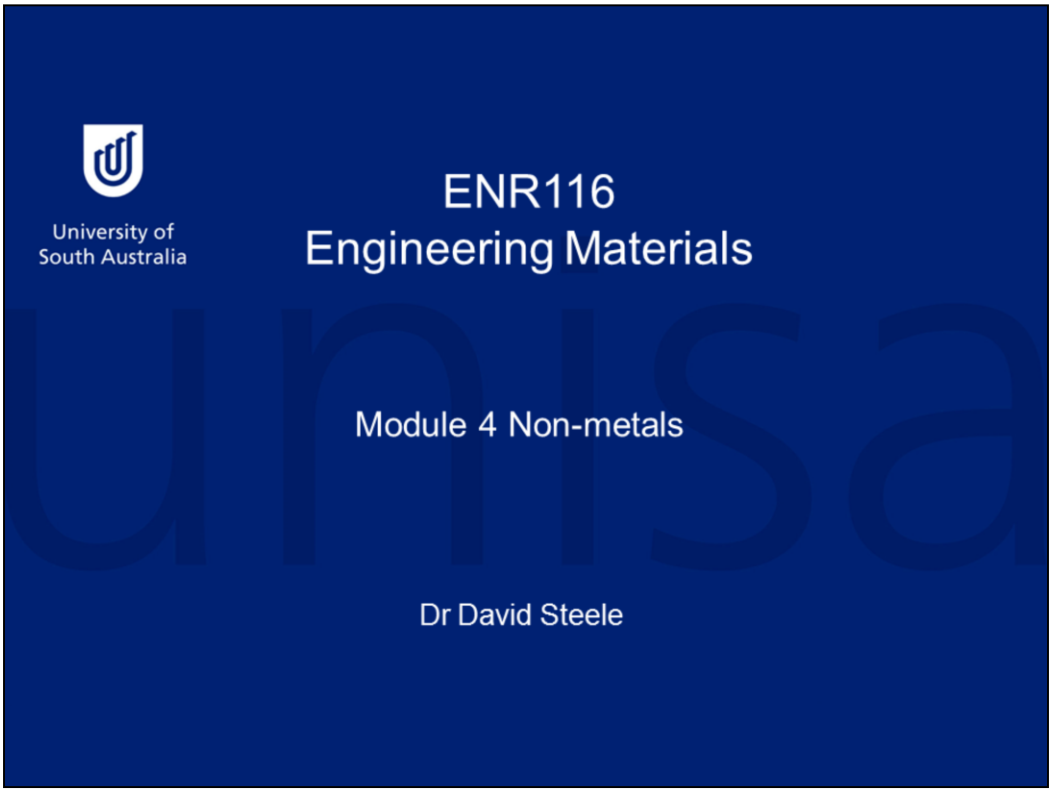

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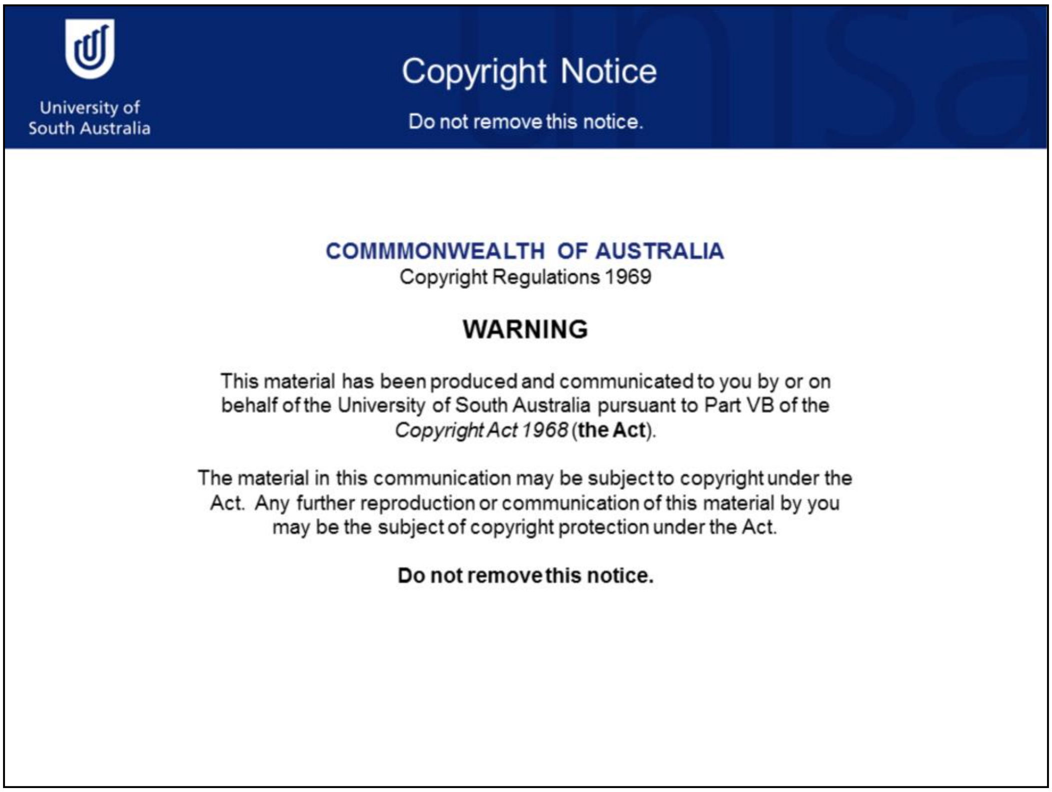
ENR116
Engineering Materials

Module 4 Non-metals

Dr David Steele

Welcome to ENR116. This lecture summary is part of module 4, non metals



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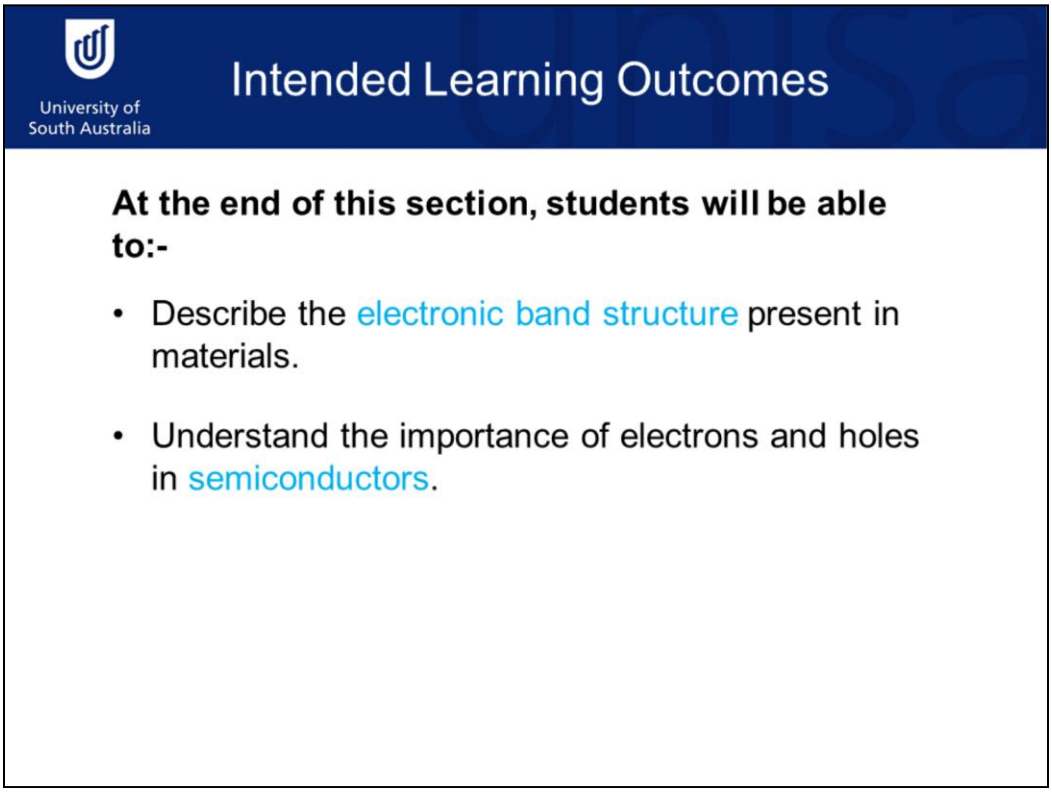
Semiconductors

Week 12C



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Intended Learning Outcomes

At the end of this section, students will be able to:-

- Describe the electronic band structure present in materials.
- Understand the importance of electrons and holes in semiconductors.

•The intended learning outcomes of this lecture summary are for students to be able to describe electronic band structure and

• understand the importance of electrons and holes in semiconductor materials.

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Semiconductors

Found in virtually every technological device

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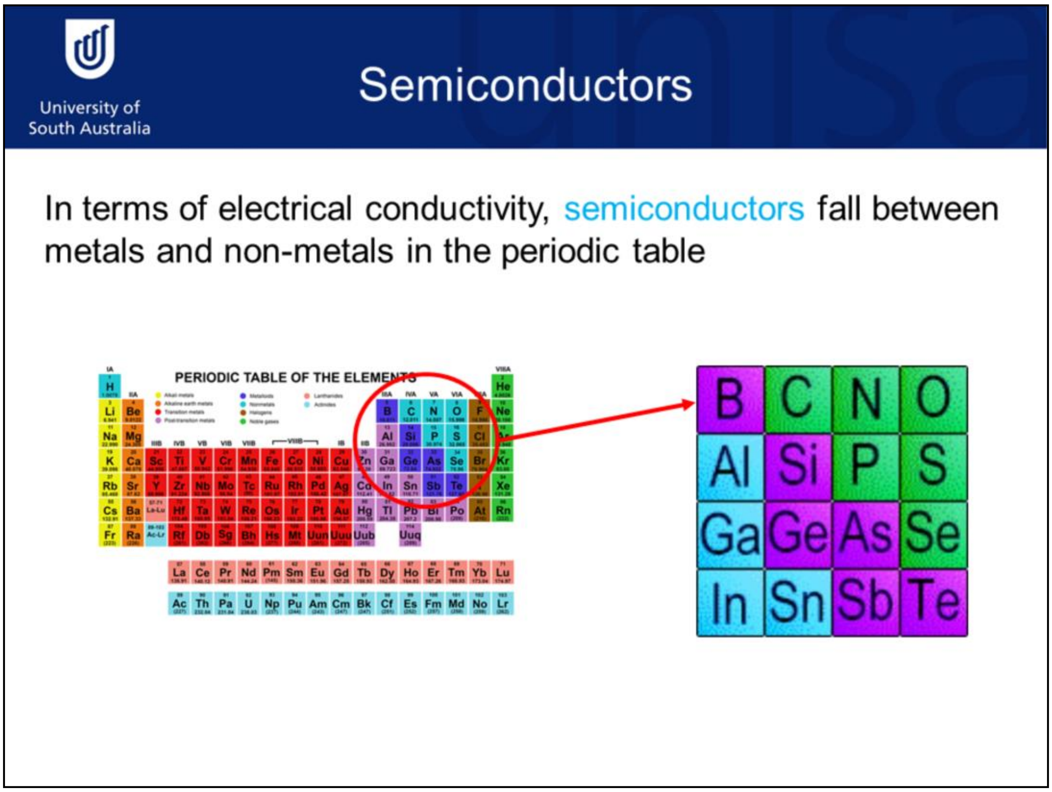
The development and utilisation of semi conductor materials have shaped the world today. Without these materials, our computers would still be housed in rooms, the possibility of green energy from the sun and entire industries from display screens to digital photography would not exist.



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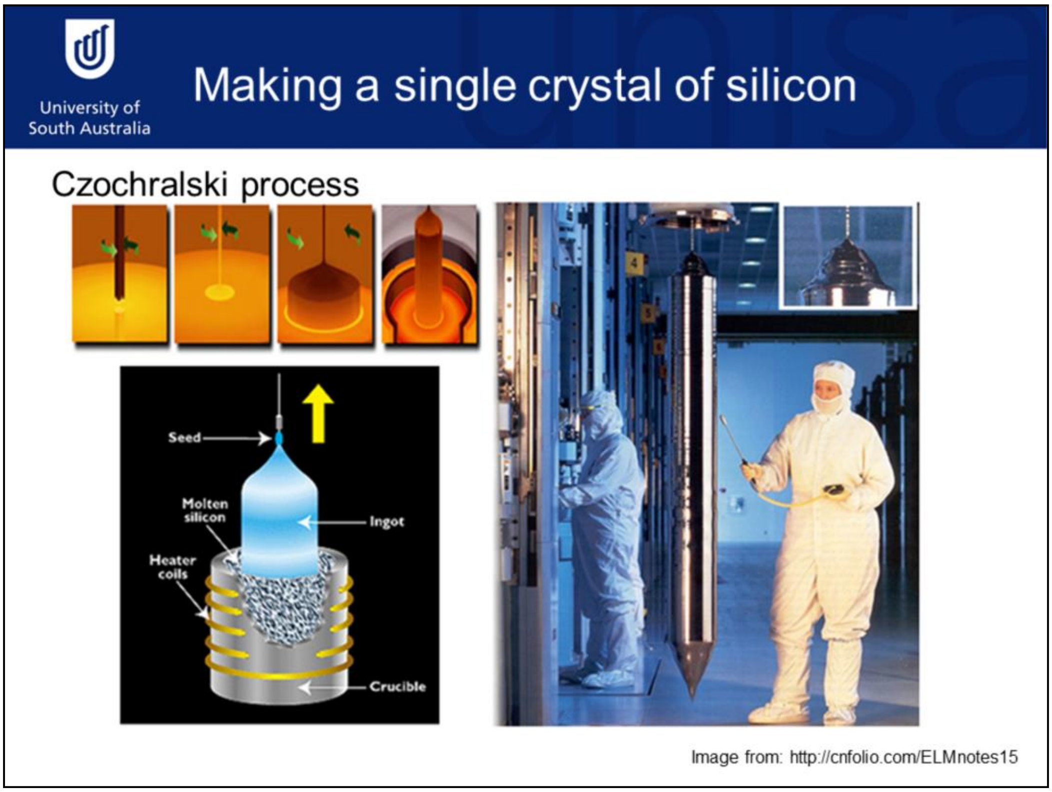
Semiconductors

In terms of electrical conductivity, semiconductors fall between metals and non-metals in the periodic table

PERIODIC TABLE OF THE ELEMENTS

B	C	N	O
Al	Si	P	S
Ga	Ge	As	Se
In	Sn	Sb	Te

In terms of electrical conductivity, the semiconducting materials lie between the metals (conductors) and non metals (insulators) on the periodic table. Shown here in purple, are the semi conducting elements silicon and geranium. These can be used in addition to compounds such as Gallium arsenide.



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Making a single crystal of silicon

Czochralski process

Image from: http://cnfolio.com/ELMnotes15

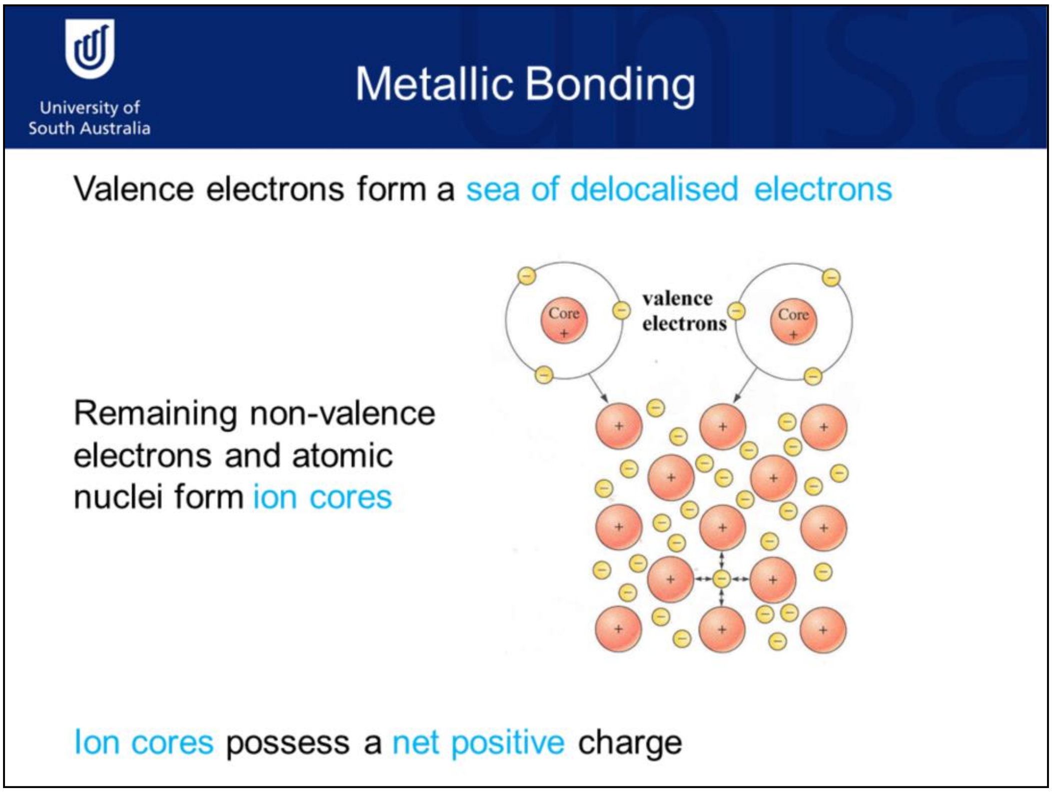
•The advances in semiconductors would not be possible without the production of extremely pure single crystals of silicon.

These single crystals are produced using the Czochralski process, which is named after the Polish scientist who developed the process.

Here the high-purity silicon is first melted in a crucible, usually made of quartz. Dopant impurity atoms such as boron or phosphorus are then added to the molten silicon, and a rod-mounted seed crystal is dipped into the melt.

The seed crystal's rod is slowly pulled upwards and rotated simultaneously.

By precisely controlling the temperature gradients, the rate of pulling and the speed of rotation a large, single-crystal, cylindrical silicon ingot can be extracted from the melt.



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Metallic Bonding

Valence electrons form a sea of delocalised electrons

Remaining non-valence electrons and atomic nuclei form ion cores

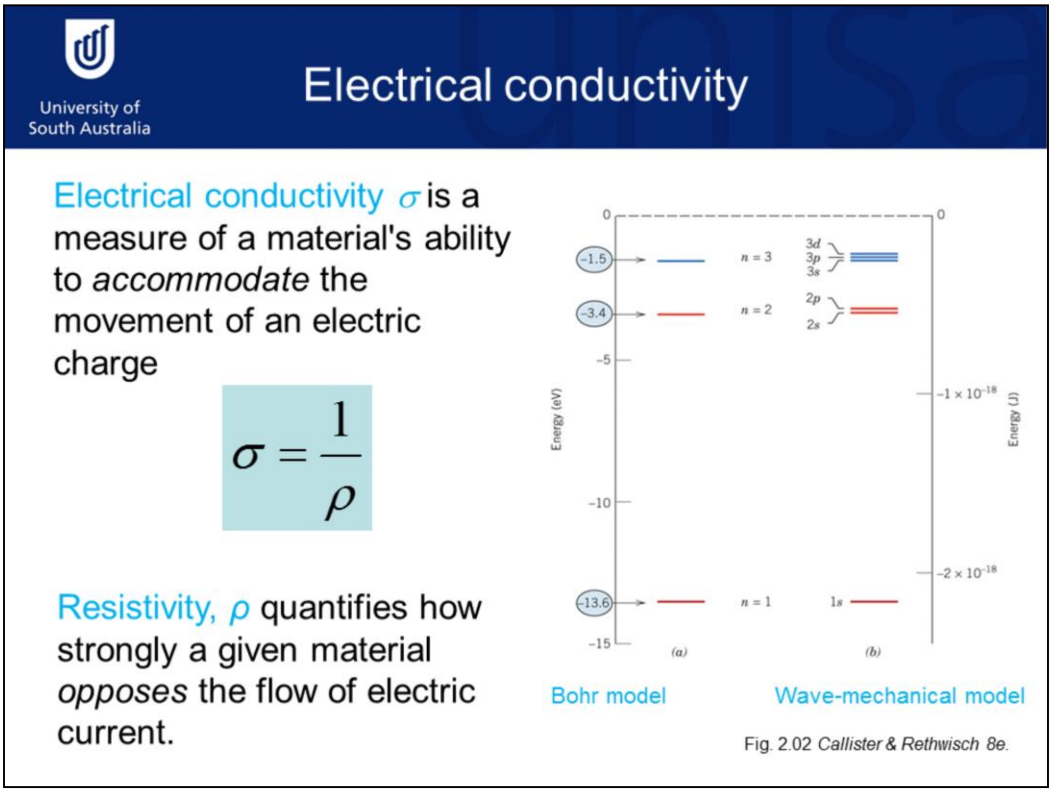
Ion cores possess a net positive charge

In order to understand how semiconducting materials work, we need to have a solid understanding of how materials conduct electricity. To do this, we'll start by briefly revising metallic bonding.

In a metal, the valence electrons are not shared between any specific or particular atoms in the solid, but rather, they are free to move throughout the metal, creating a 'sea' of delocalised electrons.

The non-valence electrons are not free to move and will stay around individual nuclei, forming what is known as an ion core. The ion cores possess a net positive charge.

The ion cores pack closely together and allow the free electrons to associate with the whole material.



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Electrical conductivity

Electrical conductivity σ is a measure of a material's ability to *accommodate* the movement of an electric charge

$$\sigma = \frac{1}{\rho}$$

Resistivity, ρ quantifies how strongly a given material *opposes* the flow of electric current.

Bohr model   Wave-mechanical model

Fig. 2.02 *Callister & Rethwisch 8e.*

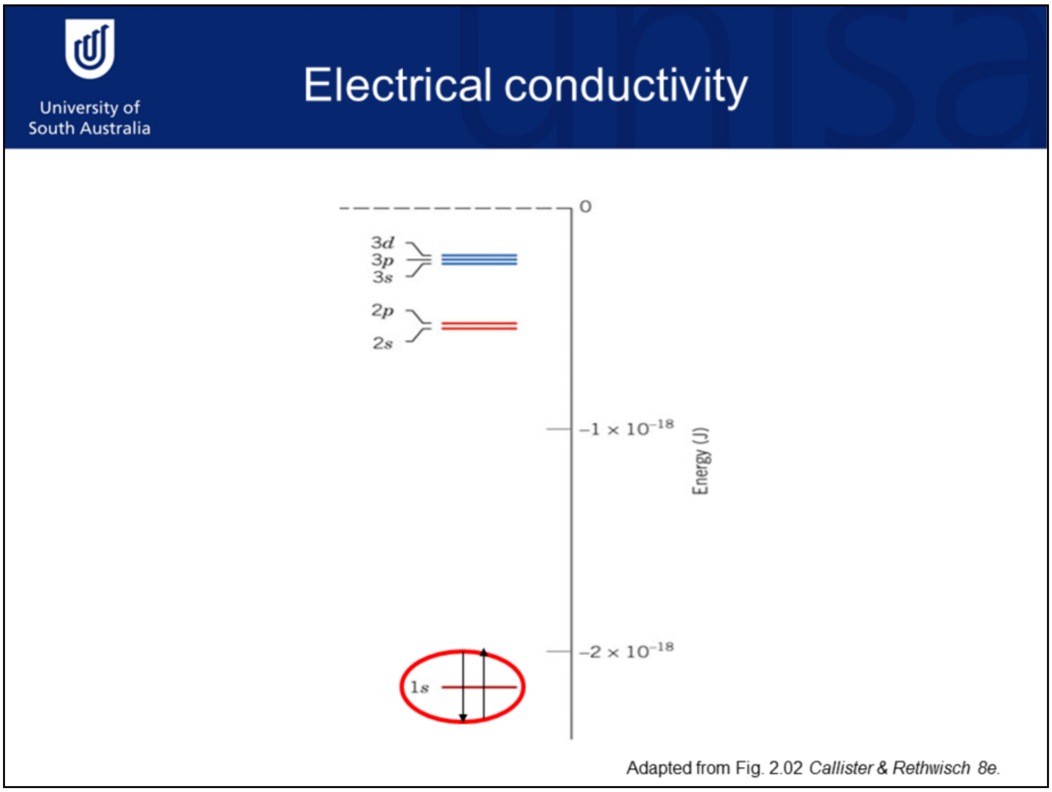
Electrical conductivity, sigma, is a measure of a material's ability to accommodate the movement of an electric charge. Mathematically, conductivity is equal to the reciprocal of the resistivity, or rho, where rho quantifies how strongly a given material opposes the flow of electric current.

At the molecular level, conduction relies on the movement of free electrons.

The number of free electrons that is available to transfer the current is dependant on electron states or levels, and their occupancy.

In a previous lecture summary we explored the concept of atomic structure.

During this the idea of electrons occupying orbitals, shells and subshells was outlined, and as revision, you can see here that there are electron shells identified as 1, 2, 3, etc. and within these, subshells s, p, d and f with 1, 3, 5 and 7 states respectively.



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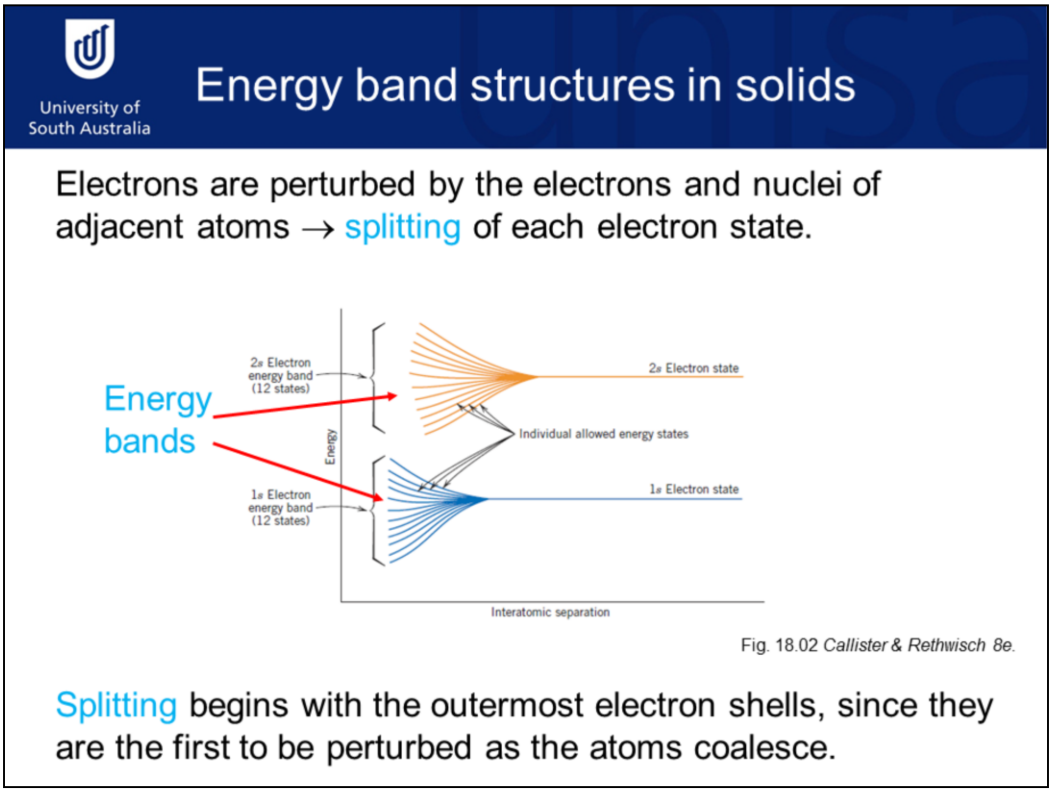
Electrical conductivity

Adapted from Fig. 2.02 *Callister & Rethwisch 8e.*

The Pauli exclusion principle describes the order and manner in which electrons fill these states. The lowest energies are occupied first and each state has a maximum of two electrons with opposite spins.

Now, whilst this atomic structure description is fine for specific, individual atoms it does not account for any effects that might occur due to proximity in a volume of solid material containing many atoms.

Given our previous discussions regarding bonding, and in particular ionic bonding, it should come as no surprise that atoms of the same element in close proximity can influence each other and perturb these electronic structures.



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Energy band structures in solids

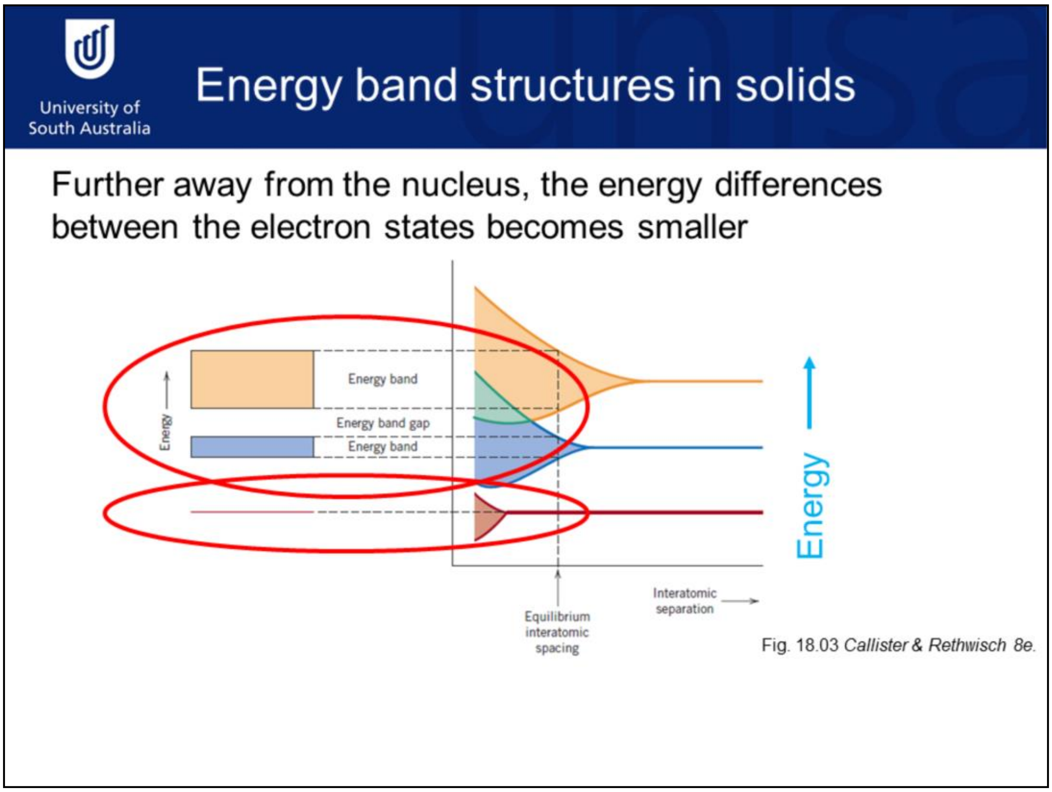
Electrons are perturbed by the electrons and nuclei of adjacent atoms → splitting of each electron state.

Fig. 18.02 *Callister & Rethwisch 8e.*

Splitting begins with the outermost electron shells, since they are the first to be perturbed as the atoms coalesce.

A general outcome of the proximity of adjacent electrons and nuclei is that each electron state can be further split to form a series of electron states; or an electron energy band.

Within these bands the difference in energy between levels is very small. The energy states are still discrete, but difference between adjacent states is exceedingly small. Splitting begins with the outermost electron shells, since they are the first to be perturbed as the atoms pack together.



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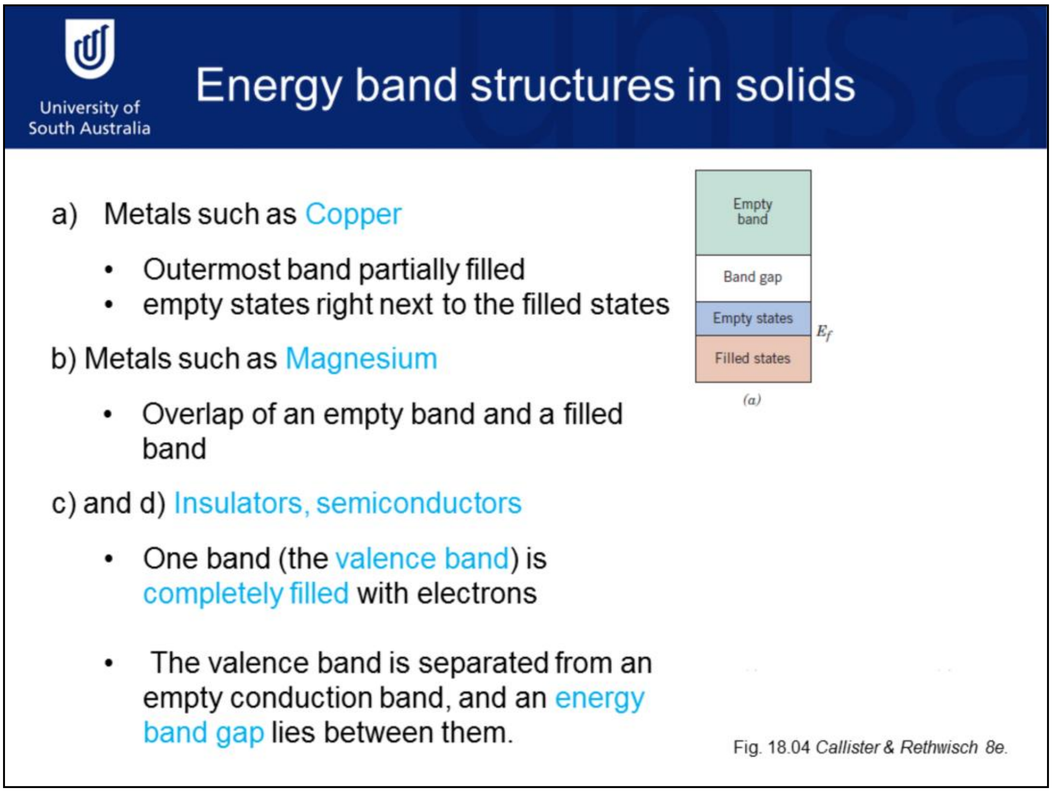
Energy band structures in solids

Further away from the nucleus, the energy differences between the electron states becomes smaller

Fig. 18.03 *Callister & Rethwisch 8e.*

As we move further away from the nucleus the energy differences between the electron states becomes smaller. This means that there are some states where the electron energy band will overlap between electron shells and you can see this in the illustration, here. This effect doesn’t happen for those shells closest to the nucleus, where there are still relatively large gaps between adjacent shells.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Energy band structures in solids

a) Metals such as Copper

- Outermost band partially filled
- empty states right next to the filled states

b) Metals such as Magnesium

- Overlap of an empty band and a filled band

c) and d) Insulators, semiconductors

- One band (the valence band) is completely filled with electrons
- The valence band is separated from an empty conduction band, and an energy band gap lies between them.

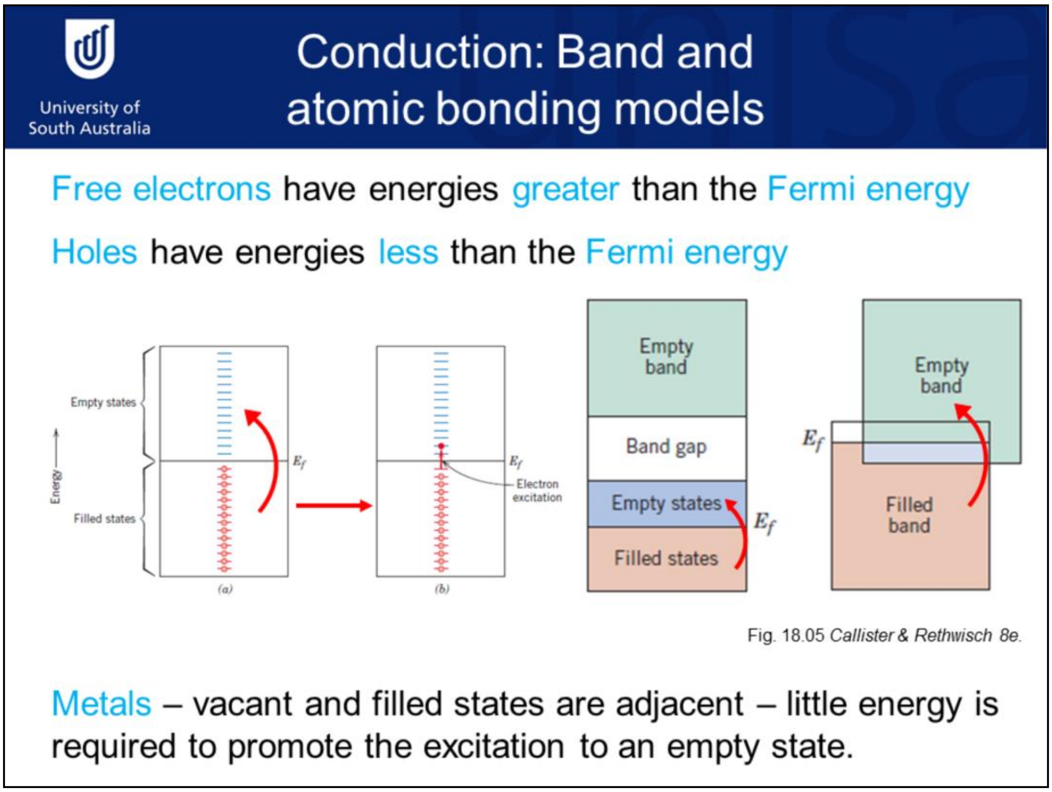
Fig. 18.04 *Callister & Rethwisch 8e.*

So, we’ll now consider in turn the situation for several types of material at absolute zero or 0 K. We consider the situation at this temperature to eliminate any possible movement of electrons due to thermal energy. There are four possible scenarios.

First, for some metals, such as copper, the band structure can be described as in image (a). These metals have one outermost band which is only partially filled by electrons, so we have some empty states right next to the filled states. E subscript f is the Fermi energy, or the energy of the highest filled state.

For other metals, such as magnesium, the electronic band structure is as shown in (b). Here there is an overlap of an empty band and a filled band. Isolated magnesium atoms have 2 3s electrons but in the solid, when energy levels split to form energy bands, the 3s and 3p bands overlap.

The final two band structures are alike in their arrangement. In both cases the valence band is completely filled with electrons but is separated from an empty conduction band by a band gap. The difference between c and d is in the size of this band gap. A large band gap, such as in c, describes **insulators** and a small band gap, such as d, characterises the **semiconductors**.



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Conduction: Band and atomic bonding models

Free electrons have energies greater than the Fermi energy

Holes have energies less than the Fermi energy

Fig. 18.05 *Callister & Rethwisch 8e.*

Metals – vacant and filled states are adjacent – little energy is required to promote the excitation to an empty state.

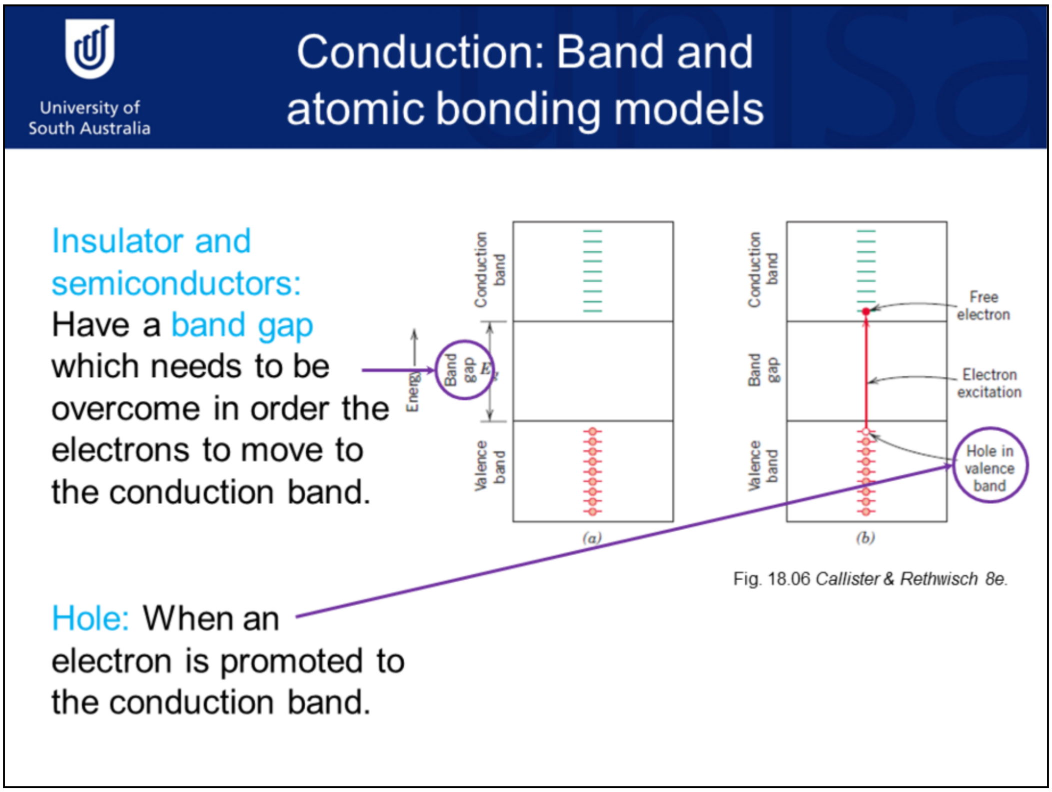
Before we finish our discussion of conduction in terms of electronic energy bands and band gaps, we need to redefine our idea of a free electron.

Whilst we recall that previously we described all the electrons in the electron cloud or sea as free electrons, we will now state that free electrons are defined as those with energies greater than the Fermi energy. Remember the Fermi energy is the energy of the highest filled electron state.

Secondly, we define a hole which has an energy less than the Fermi energy. Holes also participate in electronic conduction, and we'll come back to this concept in the next few slides.

Having defined these two terms we can now look again at the three material types; conductors, insulators and semiconductors, and redefine each in terms of what we know about electric conductivity.

So, for metals, excited electrons from the filled states are promoted straight to adjacent empty states. Very little energy is required in order to do this, and it is these electrons that conduct. You can see this situation represented in the illustrations here, for a copper like metal with a partially filled outermost band, and for a metal such as magnesium, which contains overlapping energy bands.



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Conduction: Band and atomic bonding models

Insulator and semiconductors: Have a band gap which needs to be overcome in order the electrons to move to the conduction band.

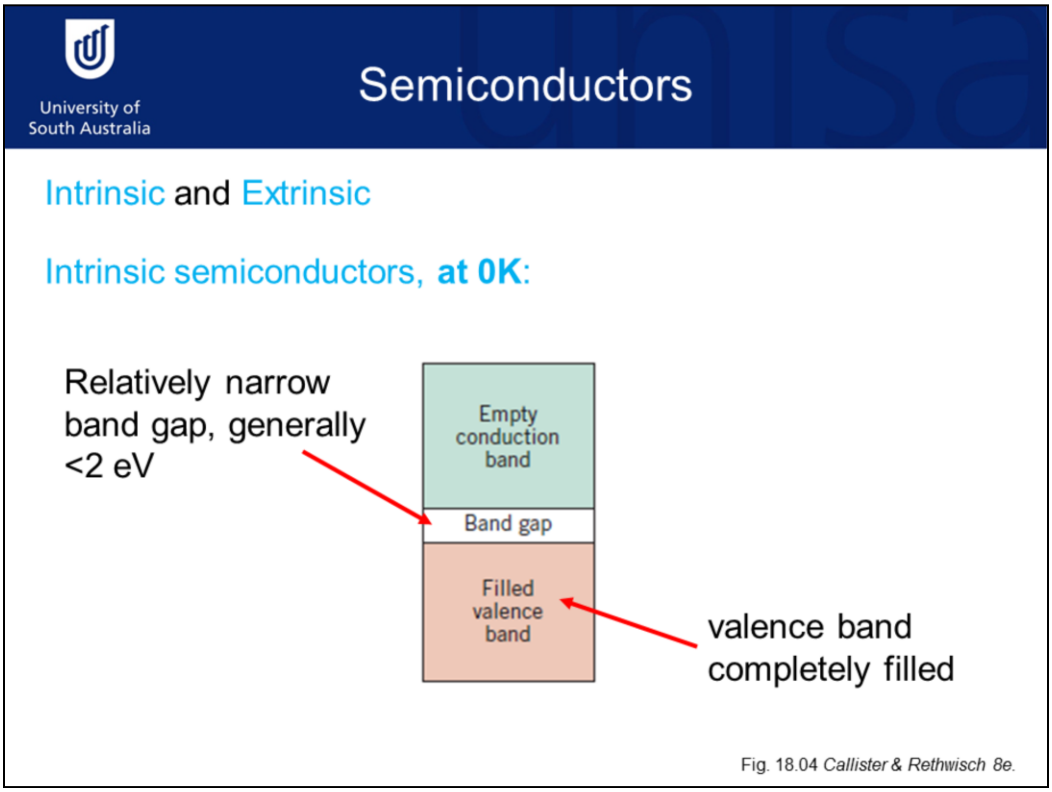
Hole: When an electron is promoted to the conduction band.

Fig. 18.06 *Callister & Rethwisch 8e.*

For insulators and semiconductors, excited electrons from the valence band do not have an adjacent state available. In order for these electrons to become free (conducting) electrons, they have to cross the band gap. This requires sufficient energy, defined by E subscript g.

The difference between a semiconductor and insulator is in this value E subscript g; for insulators this is large whilst for semiconductors Eg is small.

Note that when an electron is promoted to the conduction band, it leaves behind a ‘hole’. You’ll remember in a previous slide we defined a hole as an entity having an energy less than the Fermi energy.



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Semiconductors

Intrinsic and Extrinsic

Intrinsic semiconductors, **at 0K**:

Relatively narrow band gap, generally <2 eV

Empty conduction band

Band gap

Filled valence band

valence band completely filled

Fig. 18.04 *Callister & Rethwisch 8e.*

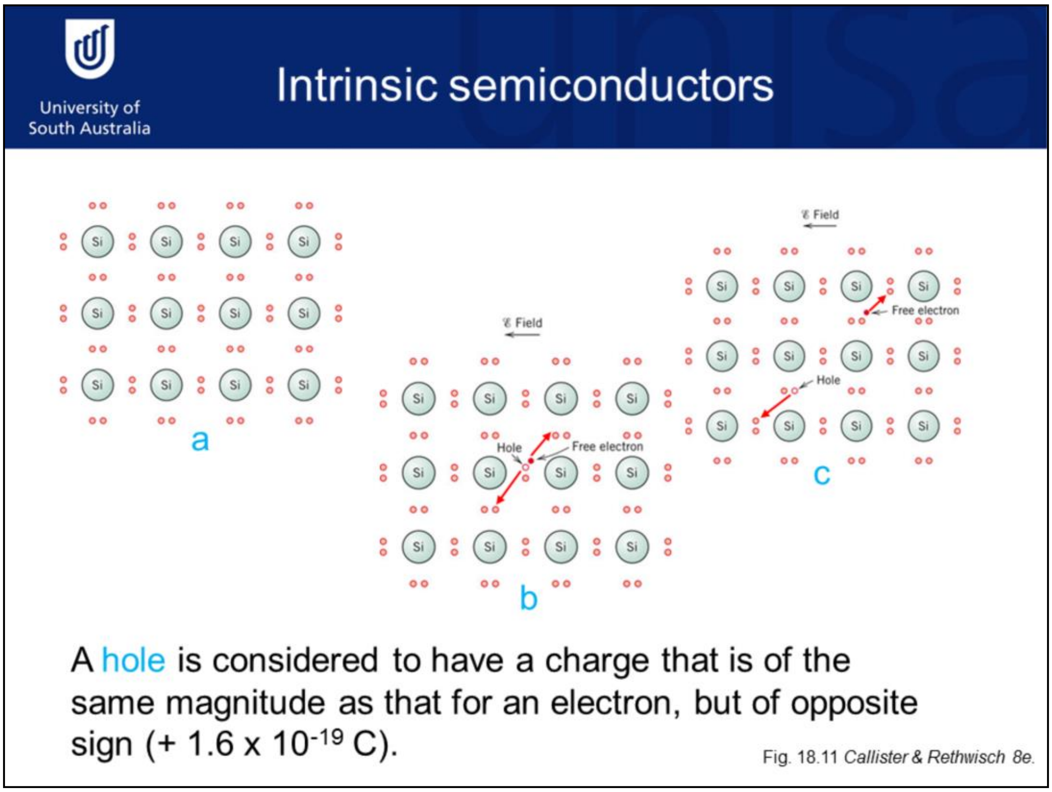
Now that we've established how conduction works in terms of electronic energy bands for different material types, we'll focus for the rest of this summary on semiconductor materials.

There are essentially two types of semiconductor; intrinsic and extrinsic.

Intrinsic semiconductors have electrical properties which stem from the electronic structure inherent to the material. For extrinsic semiconductors, the electrical properties are the result of impurity atoms.

Intrinsic semiconductors have an electronic band structure such as this one, with a band gap of less than 2 electron volts, and a filled valance band.

There are two elemental semiconductors in addition to a number of compounds. Silicon (Si) and germanium (Ge) are the two elemental semiconductors, with band gap energies of approximately 1.1 and 0.7 eV, respectively. Gallium arsenide (GaAs), indium antimonide (InSb), cadmium sulfide (CdS), telluride (ZnTe) are intrinsic semiconductor compounds.



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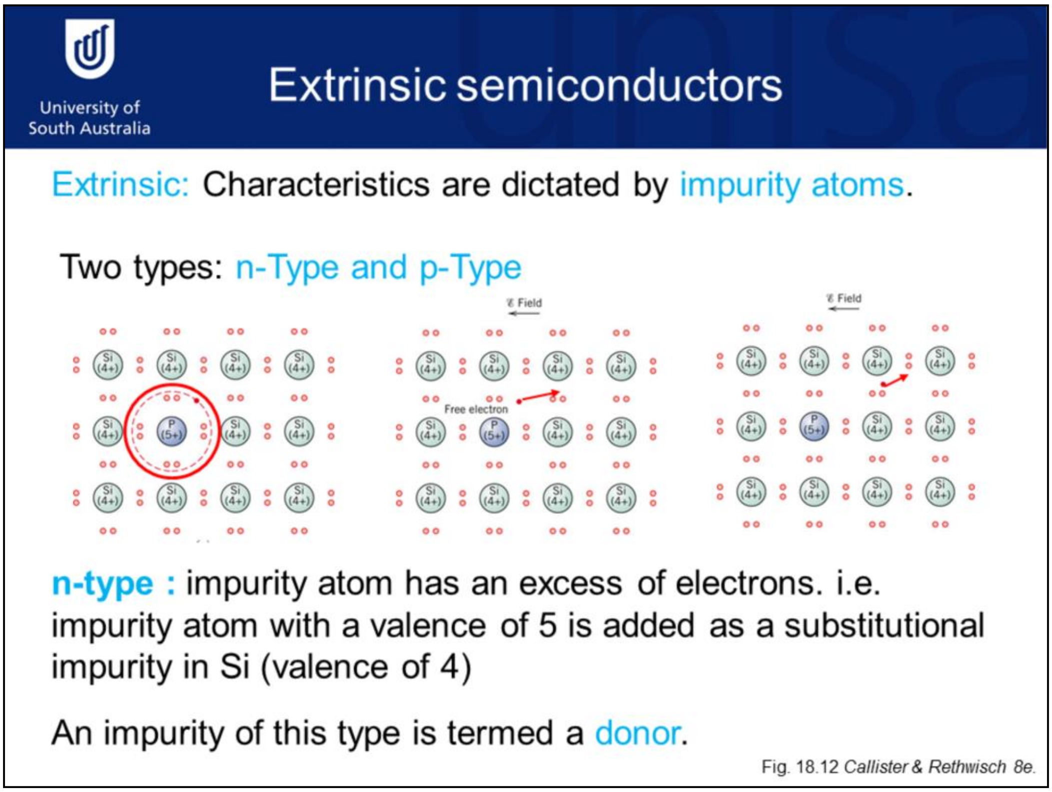
Intrinsic semiconductors

A hole is considered to have a charge that is of the same magnitude as that for an electron, but of opposite sign (+ 1.6 x 10^{-19} C).

Fig. 18.11 *Callister & Rethwisch 8e.*

For intrinsic semiconductors, electrical conduction occurs when an electron is excited into the conduction band and leaves behind a missing electron – a vacant electron state in the valence band - in one of the covalent bonds. You can see this process in image b, here.

- The conductivity in an external electric field can then be understood in terms of the electron moving in one direction whilst the hole moves in the opposite direction, as shown in c. The hole is considered to have a charge that is of the same magnitude as that for an electron, but of opposite sign (+ 1.6 x 10^{-19} C).



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Extrinsic semiconductors

Extrinsic: Characteristics are dictated by impurity atoms.

Two types: n-Type and p-Type

n-type : impurity atom has an excess of electrons. i.e. impurity atom with a valence of 5 is added as a substitutional impurity in Si (valence of 4)

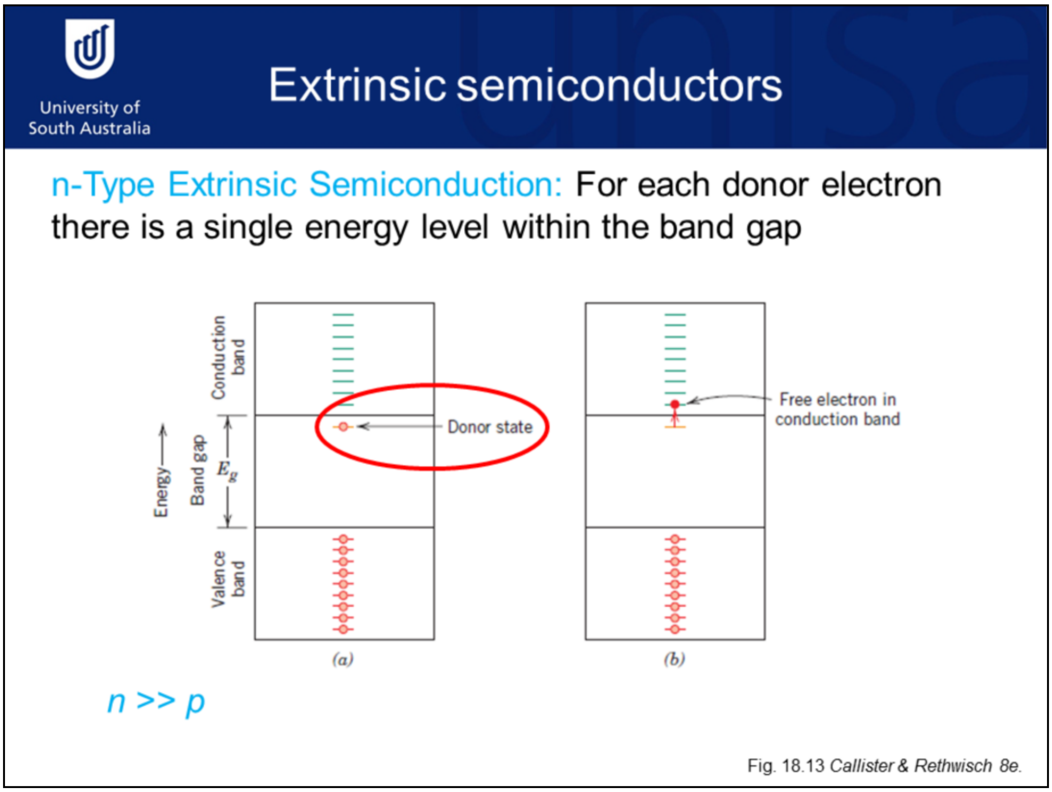
An impurity of this type is termed a donor.

Fig. 18.12 *Callister & Rethwisch 8e.*

Commercially, by far and away the most common semiconductors are extrinsic semiconductors.

These are so called ‘doped’ semiconductors; here impurity atoms are deliberately added to introduce either excess electrons or excess holes. For example, an impurity concentration of one atom in 1012 is sufficient to render silicon extrinsic at room temperature.

There are two types of extrinsic semiconductor, n-type and p-type. N-type extrinsic semiconductors are those where the impurity atom has an excess of electrons i.e. phosphorous in silicon, as seen here. Phosphorous has 5 valence electrons compared to silicon’s 4 and so can provide a free electron. Impurities of this type are known as donors. Other potential donors are other Group VA elements.



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Extrinsic semiconductors

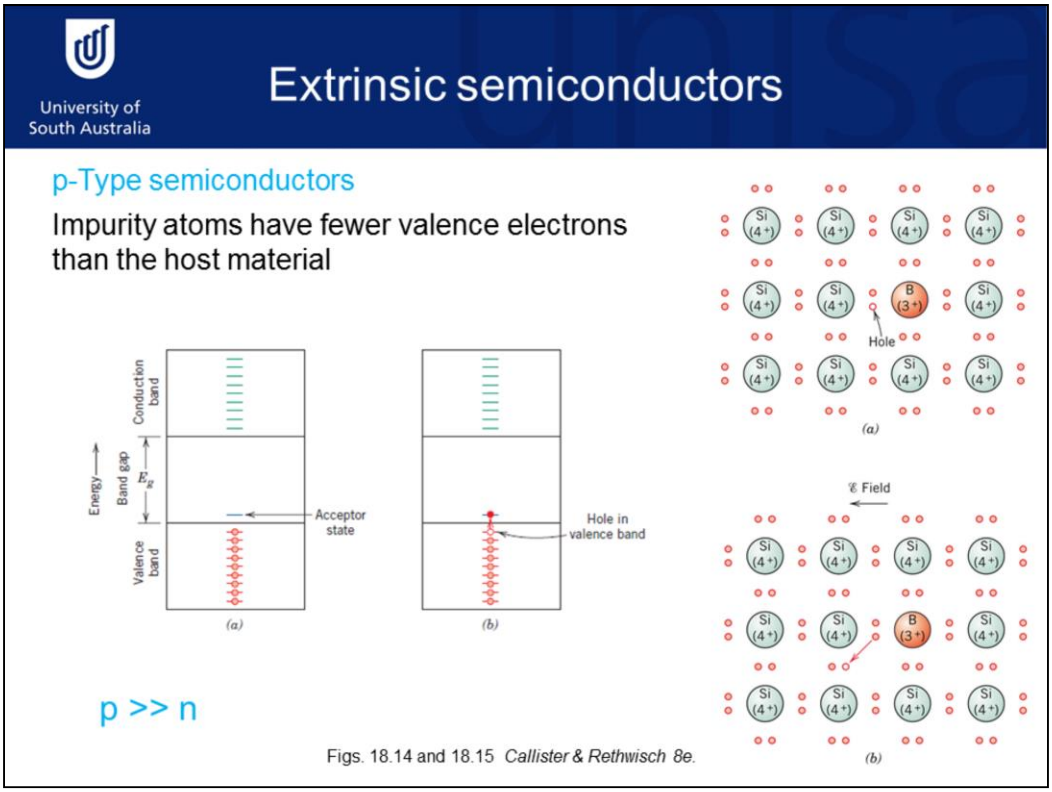
n-Type Extrinsic Semiconduction: For each donor electron there is a single energy level within the band gap

$n >> p$

Fig. 18.13 *Callister & Rethwisch 8e.*

In n-type conductors, the loosely bound donor electron exists in a single energy level located within the forbidden band gap, just below the conduction band. The energy required to promote the donor electron from this state is very much smaller than the energy required to promote one of the valence electrons. Also, because the electron is excited from this impurity level, no hole is created within the valence band.

Even at room temp there’s sufficient thermal energy to create a number of these free donor electrons, and so the number of free electrons in the conduction band is very much greater than the number of holes in the valance band, or n >> p, where n is the carrier concentration and p is the number of holes per cubic meter.



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Extrinsic semiconductors

p-Type semiconductors

Impurity atoms have fewer valence electrons than the host material

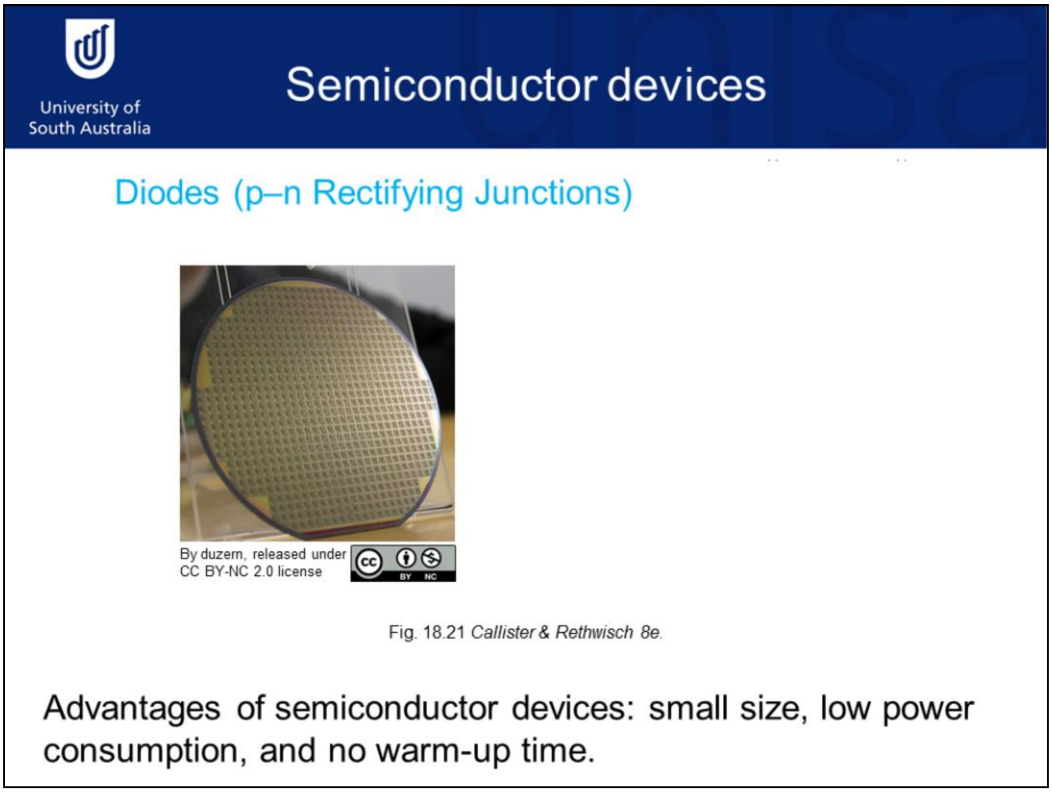
p >> n

Figs. 18.14 and 18.15 *Callister & Rethwisch 8e.*

In p-type semiconductors, impurity atoms such as boron are used. These impurities have fewer valence electrons than the host, in this case silicon. Aluminium or gallium, which are also from group IIIA of the periodic table, may also be used to dope p type semiconductors.

Each impurity atom of this type introduces an energy level within the band gap, above but very close to the top of the valence band. An impurity of this type is called an acceptor, because it is capable of accepting an electron from the valence band, leaving behind a hole.

These then provide the holes and under an applied electric field the hole accepts an electron. These holes are much more numerous than the electrons and hence, for p type semicoductors, p >> n.



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Semiconductor devices

Diodes (p–n Rectifying Junctions)

Fig. 18.21 *Callister & Rethwisch 8e.*

Advantages of semiconductor devices: small size, low power consumption, and no warm-up time.

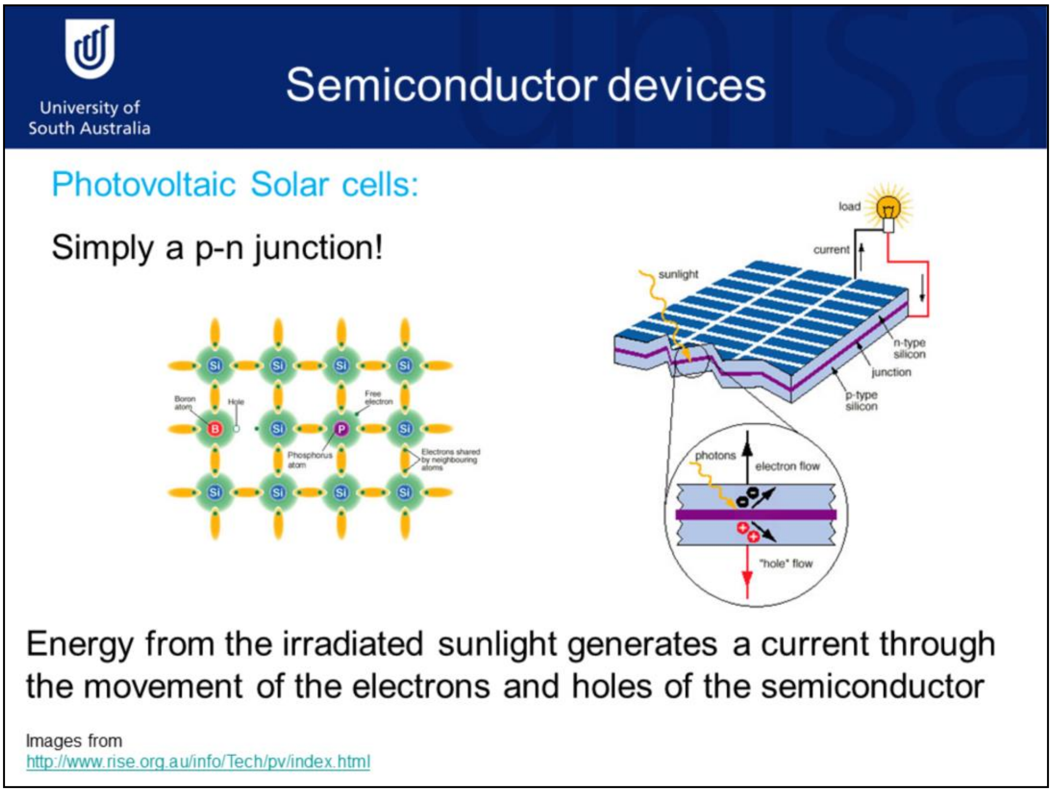
We began this lecture summary with some of the commonplace electronic products that utilise semiconductors, and we are going to finish it by briefly identifying some devices that rely on these materials to form diodes, or p-n rectifying junctions, and transistors.

A diode is a device that allows a current to flow in one direction only. Prior to the discovery of semiconductors these were fabricated from vacuum tubes, but nowadays a p-n junction may be formed from a single piece of silicon crystal. Doping on one side of the crystal creates an electron rich n-type, whilst doping on the other creates the hole rich p-type. T

his is shown in the illustration here.

When we apply a voltage across the p-n junction, this distribution of electrons and holes changes. Here the negative n-type side of the diode is attached to the negative end of a circuit and the P-type side to the positive end. The electrons in the N-type material are attracted to the positive electrode, whilst the holes flow the other way. As the holes and electrons encounter each other, they recombine and annihilate, generating energy.

Now, we were to reverse the circuit, with the N-type side connected to the positive end of the circuit and the P-type side connected to the negative end, current cannot flow. This reserve bias situation is shown here. The negative electrons are attracted to the positive electrode, and the holes to the negative electrode, away from each other, and hence the junction is now highly insulative.



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Semiconductor devices

Photovoltaic Solar cells:

Simply a p-n junction!

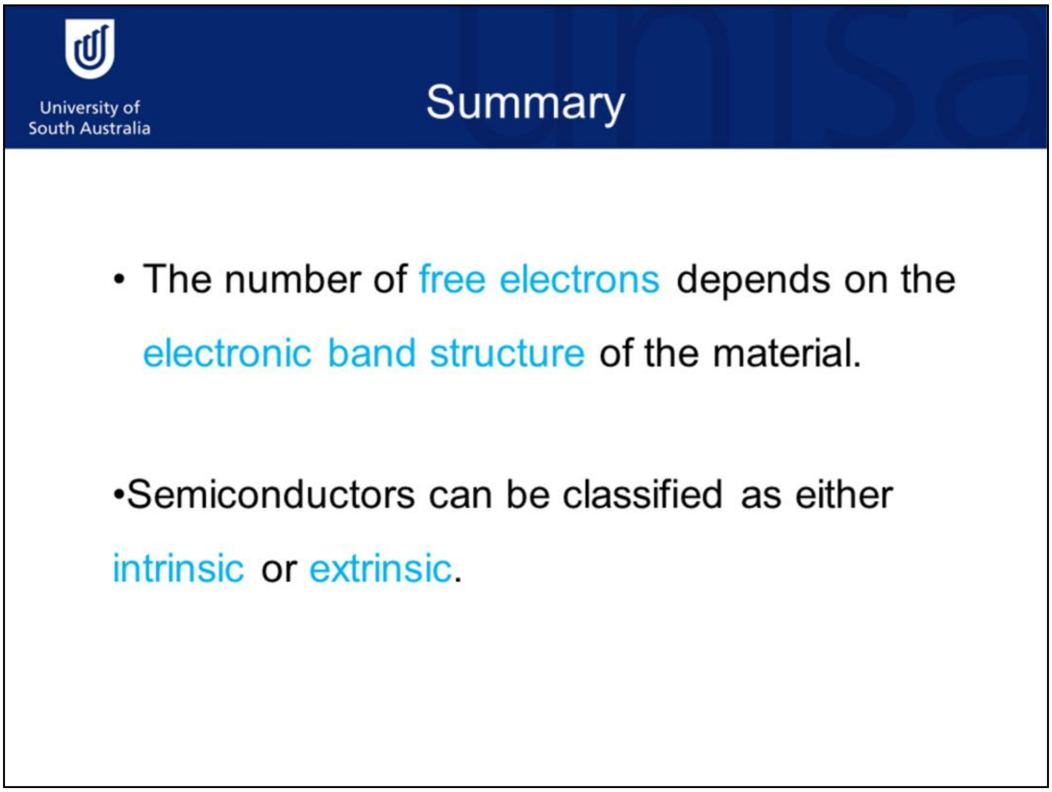
Energy from the irradiated sunlight generates a current through the movement of the electrons and holes of the semiconductor

Images from http://www.rise.org.au/info/Tech/pv/index.html

The same principles are used to construct photovoltaic solar cells and solar panels.

Solar panels are comprised of many cells containing p-n junction semiconductors. When sunlight shines on the cells, photons hit the surface and transfer their energy to the electrons in the hole rich, p-type layer. These electrons then use this energy to transfer across the junction into the n-type layer and generate a current. The cells therefore provide energy, provided the original photon energy exceeds that of the band gap.

Whilst an excellent source of green energy the efficiency of solar cells is still low, approximately 20%, and improvement of this is the subject of much ongoing research.



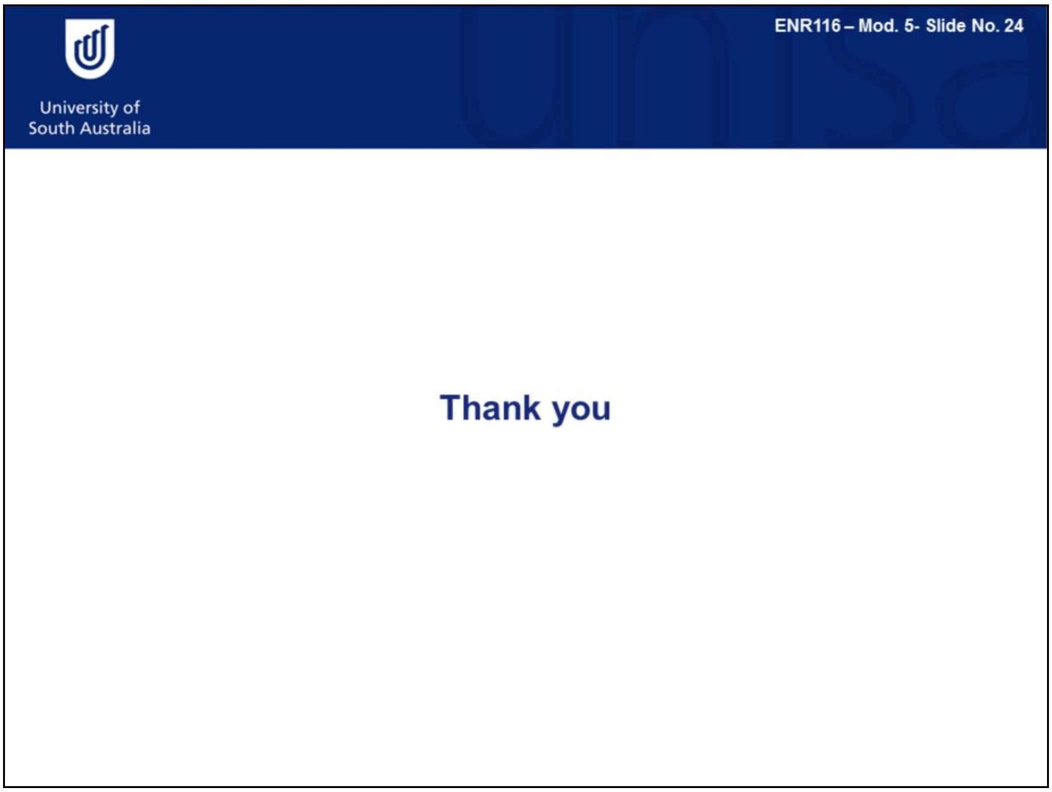
Summary

- The number of free electrons depends on the electronic band structure of the material.

•Semiconductors can be classified as either intrinsic or extrinsic.

•In summary, we have seen that the number of free electrons depends on the electronic band structure of the material, and

Semiconductors can be classified as either intrinsic or extrinsic.



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Thank you

If you have any questions or desire further clarification please post a question or comment on the Engineering Materials Discussion Forum.