

CENTRE FOR DOCTORAL TRAINING
NEW AND SUSTAINABLE
PHOTOVOLTAICS

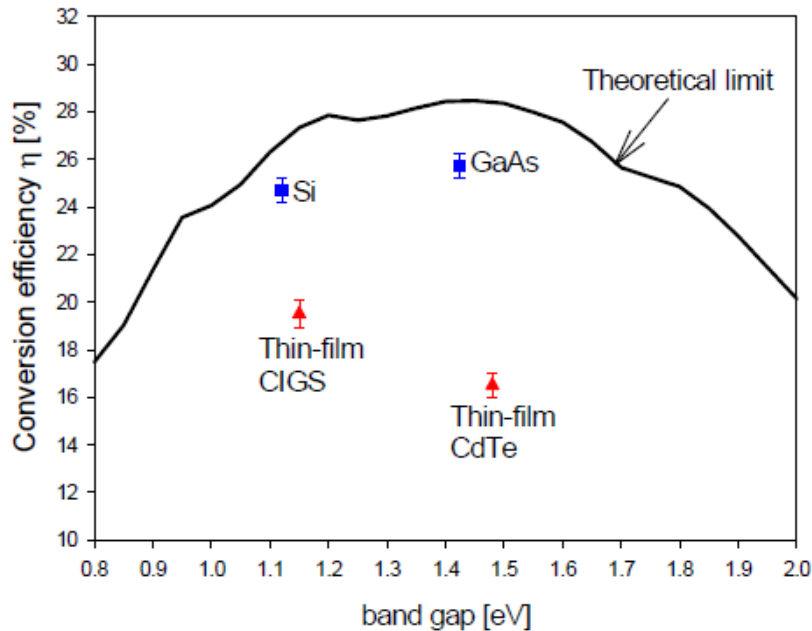
Lecture: Semiconductors and recombination

Outline – semiconductors and recombination

1. Band gap representations
2. Types of semiconductors
 - Adamantine semiconductors (Hume -Rothery 8-N co-ordination rule)
 - Others
 - Solid solutions
3. Doping and point defects
4. Generation and recombination

1. Band gap and its representation

Shockley – Queissler limit and band gap



1.1 Band gap origins

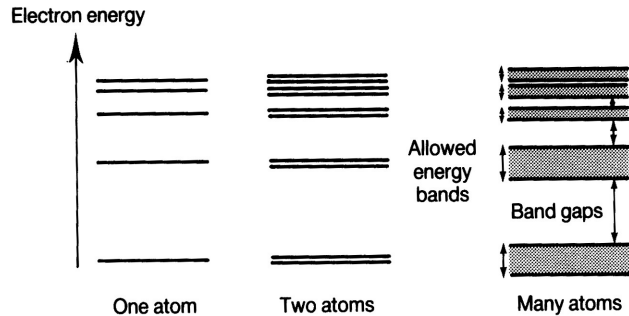
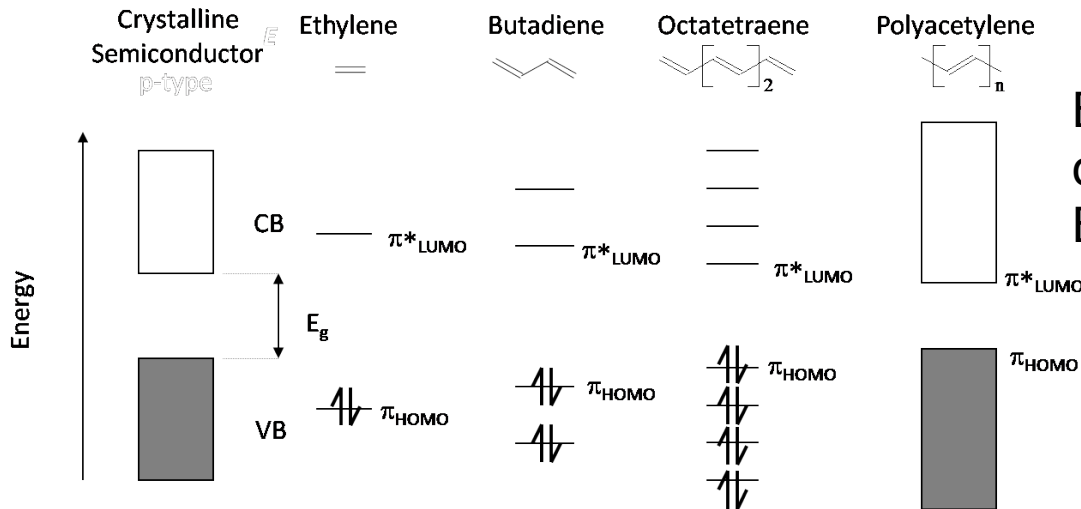
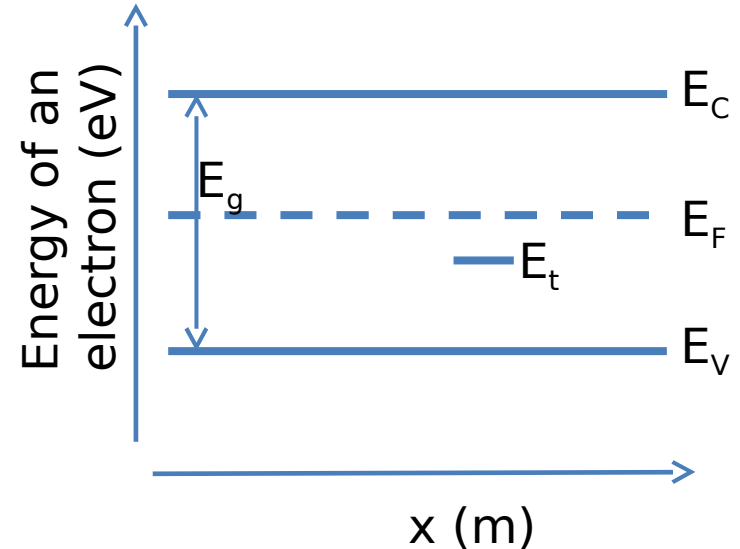


Diagram from M J Cooke Semiconductor devices

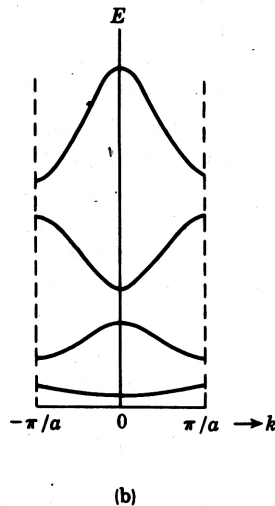
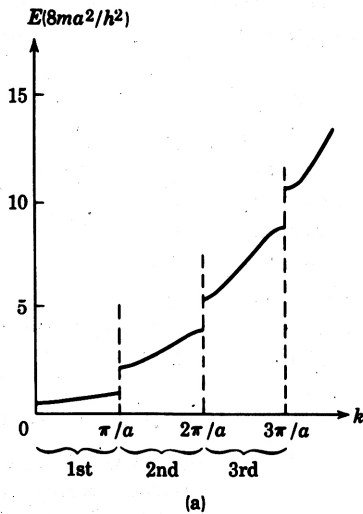
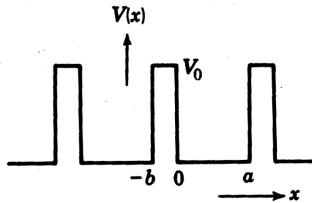
(Recall the Pauli exclusion principle)



Energy vs space representation of a band diagram.
 E_t is a trap energy level

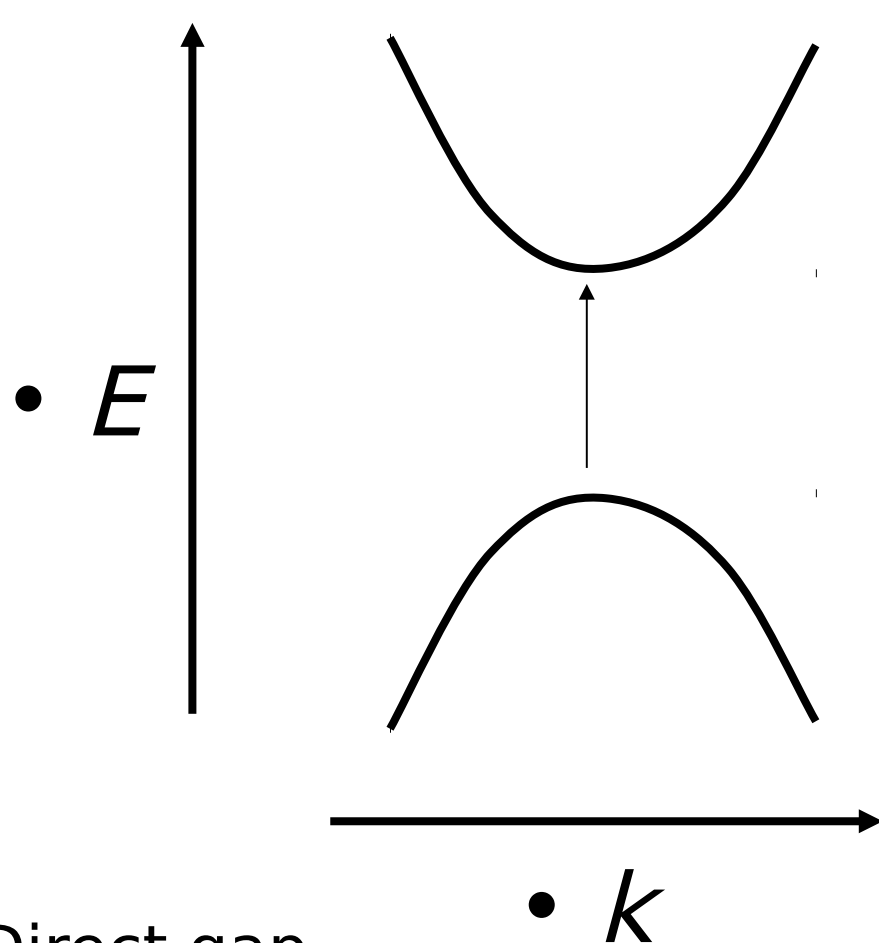
<http://photonicswiki.org/images/thumb/2/22/Homocontrol.png/800px-Homocontrol.png>

1.1 Band gap origins

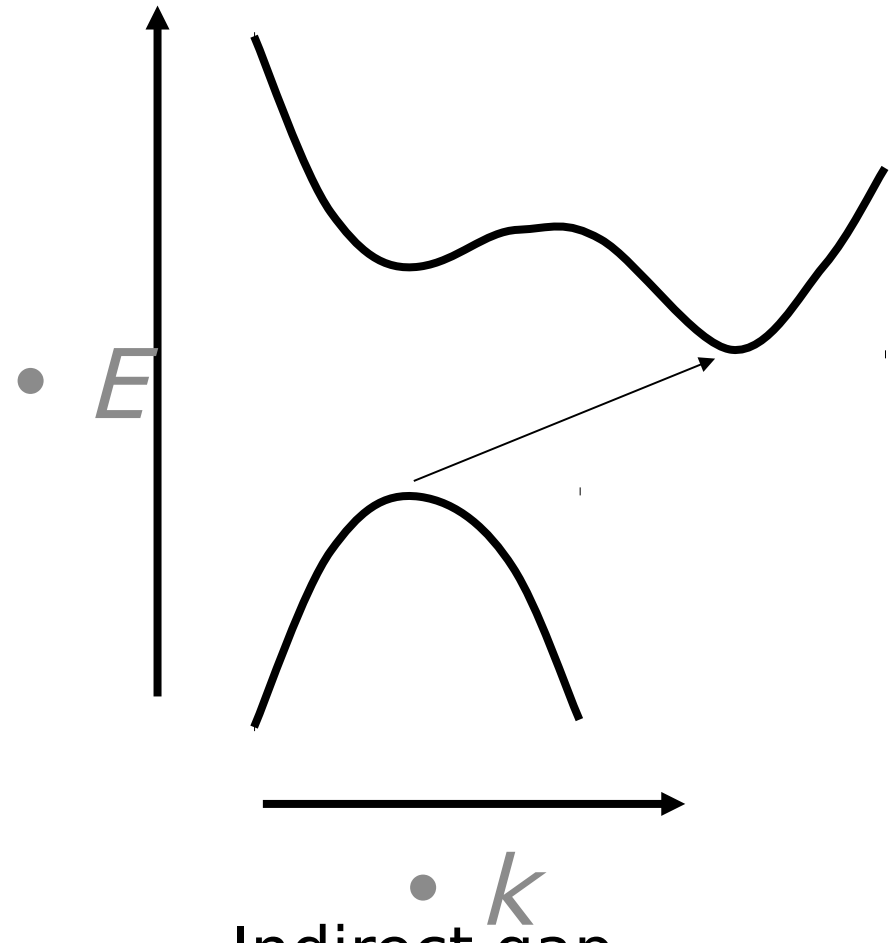


Electrons in a periodic potential
(e.g. Kronig-Penney model)

1.2 E - k reduced zone representation (textbook)

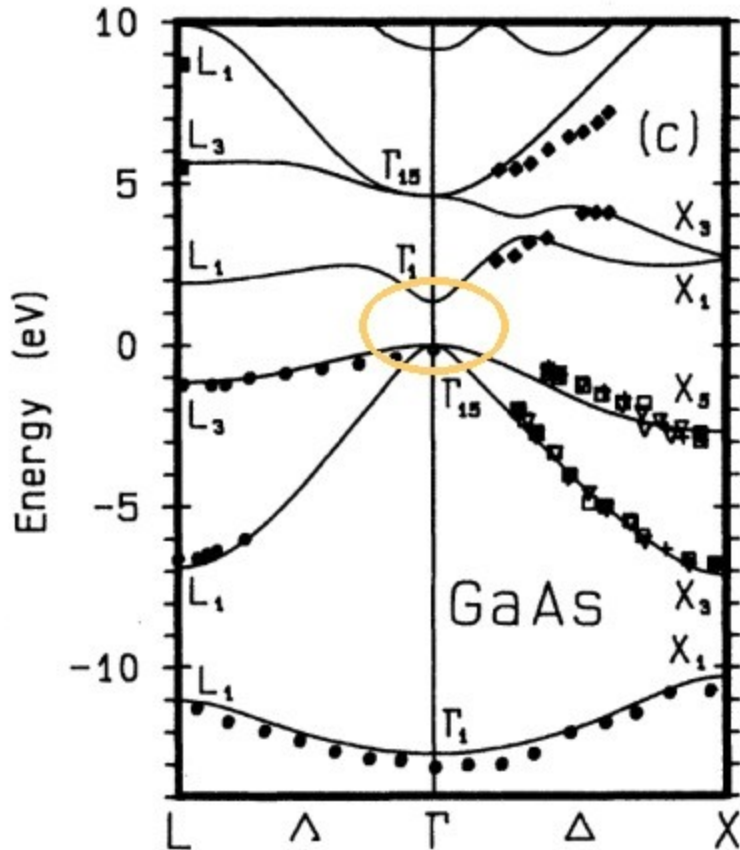


Direct gap
e.g. III-V's and II-VI's

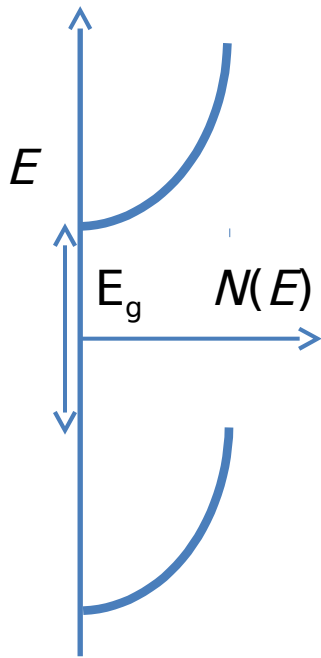


Indirect gap
e.g. Si

1.2 $E - k$ band diagram (GaAs)



1.2 $N(E)$ vs E – density of states



- NB – there is a very low DOS at the band edge and so photons of energy E_g are not the most likely to be absorbed

2 Types of semiconductor + solid solutions

Ib	IIb	III	IV	V	VI	VII
		B	C	N	O	F
		Al	Si	P	S	Cl
Cu	Zn	Ga	Ge	As	Se	Br
Ag	Cd	In	Sn	Sb	Te	I

Hume-Rothery 8-N
Co-ordination rule:

The co-ordination
number
in a compound is 8-
N,
where N is the
average
valency number.

We will use this rule to go looking for semiconductors like silicon, valency 4
i.e. isoelectronic variants of Si.

Si and **Ge** are gpIV semiconductors and are tetrahedrally co-ordinated,
they have the structure of diamond.

•Adamantine = diamond like

2 Types of semiconductor + solid solutions

III-V semiconductors

Ib	IIb	III	IV	V	VI	VII
		B	C	N	O	F
		Al	Si	P	S	Cl
Cu	Zn	Ga	Ge	As	Se	Br
Ag	Cd	In	Sn	Sb	Te	I

GaP, **GaAs**, GaSb, **InP**, InAs, InSb etc

2 Types of semiconductor + solid solutions

II-VI semiconductors

Ib	IIb	III	IV	V	VI	VII
		B	C	N	O	F
		Al	Si	P	S	Cl
Cu	Zn	Ga	Ge	As	Se	Br
Ag	Cd	In	Sn	Sb	Te	I

ZnO, ZnS, ZnSe, ZnTe, CdO, **CdS**, CdSe, **CdTe** etc

2 Types of semiconductor + solid solutions

I-III-VI semiconductors – the chalcopyrite family

Ib	IIb	III	IV	V	VI	VII
		B	C	N	O	F
		Al	Si	P	S	Cl
Cu	Zn	Ga	Ge	As	Se	Br
Ag	Cd	In	Sn	Sb	Te	I

CuInSe_2 , **CuGaSe_2** , **CuInSe_2** etc

2 Types of semiconductor + solid solutions

I-II-IV-VI semiconductors – the kesterite family

Ib	IIb	III	IV	V	VI	VII
		B	C	N	O	F
		Al	Si	P	S	Cl
Cu	Zn	Ga	Ge	As	Se	Br
Ag	Cd	In	Sn	Sb	Te	I

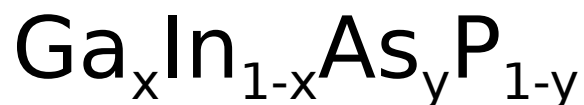
$\text{Cu}_2\text{ZnGeSe}_4$, **$\text{Cu}_2\text{ZnSnS}_4$** , $\text{Cu}_2\text{ZnSnSe}_4$ etc

Solid solutions

- GaP $E_g \sim 2.3\text{eV}$
- GaAs $E_g \sim 1.4\text{eV}$
- Ternary semiconductor $\text{Ga}(\text{As}_x\text{P}_{1-x})$ – E_g in the range 1.4 – 2.3eV

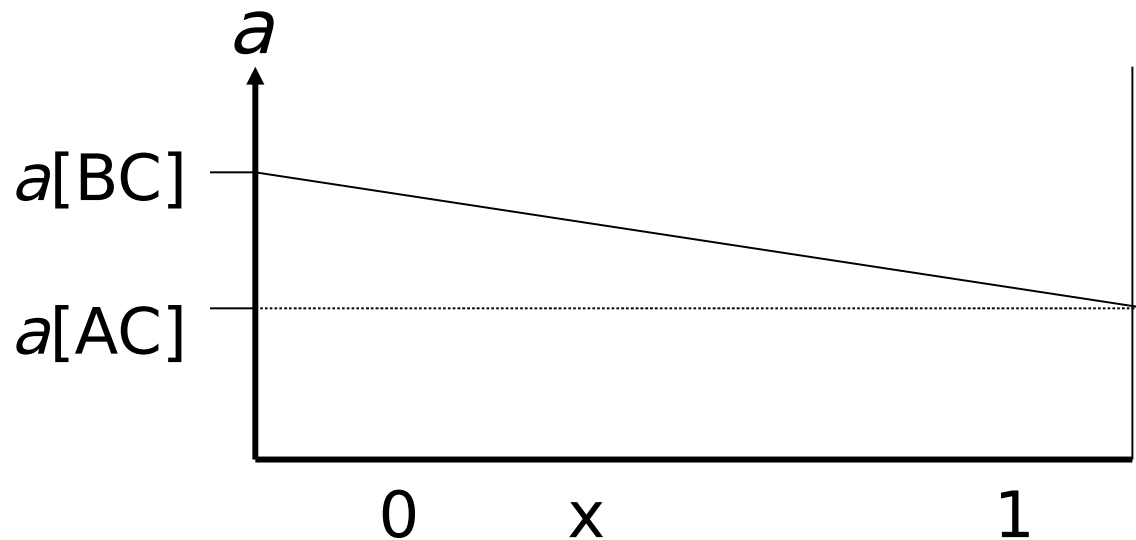
Lattice parameter (a_0) varies also

NB To vary E_g and a_0 independently, you need a quaternary system, such as



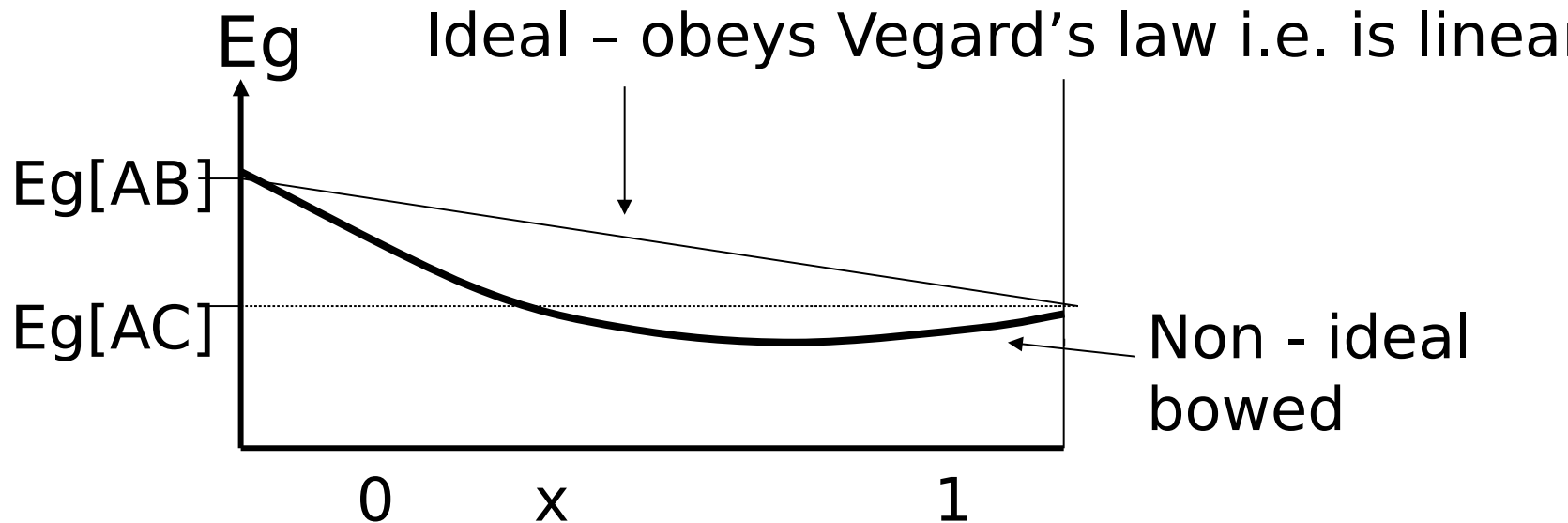
Vegards law - linear variation of lattice parameter with x

$$a[A_xB_{1-x}C] = a[BC] - x * \{a[BC] - a[AC]\}$$



Psst!
It might not
be linear in
Practice
but it often is.

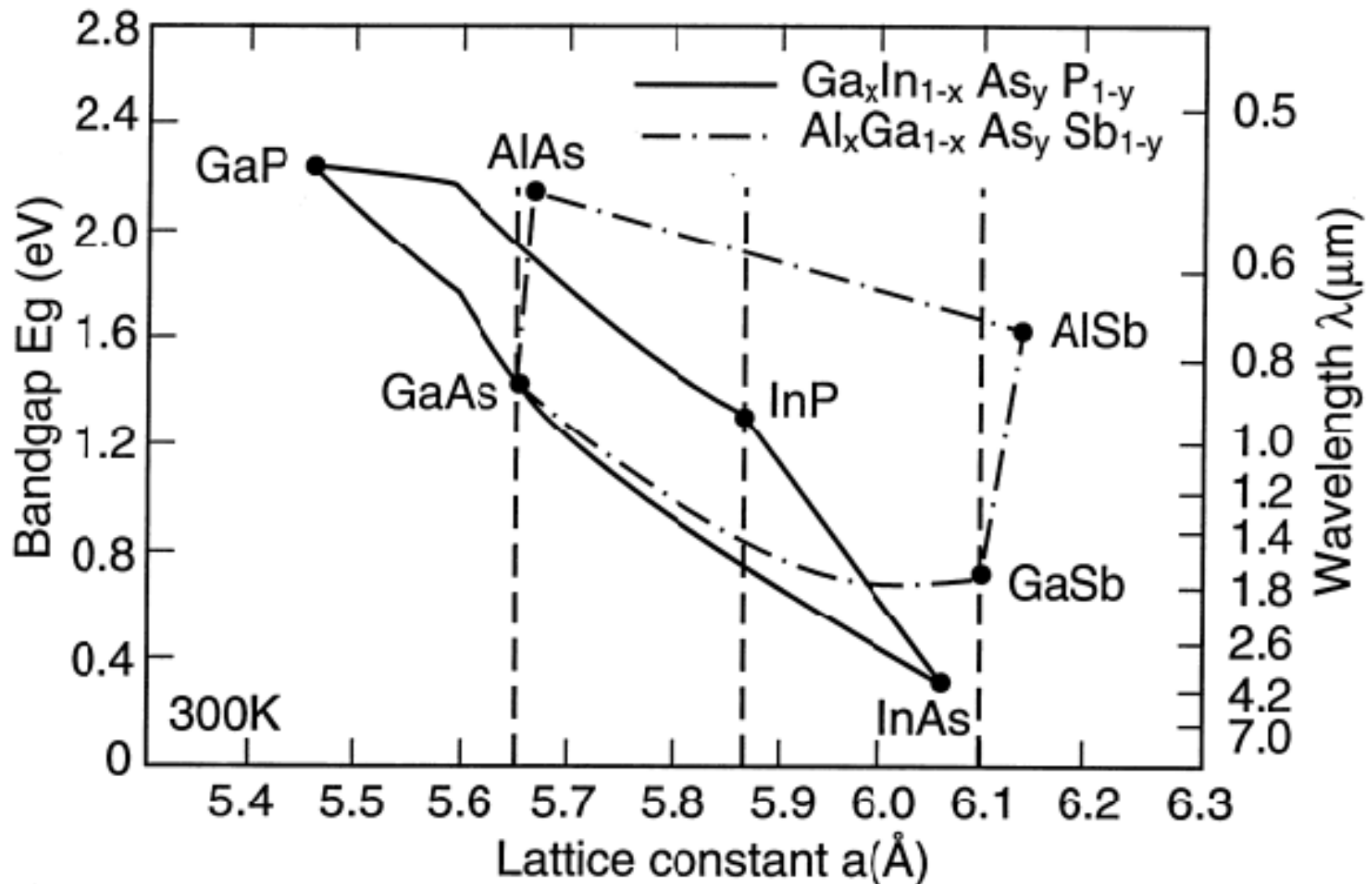
‘Vegard’s law for band gap’



Bowed curve represented by a bowing parameter 'b'

$$E_g[A_xB_{1-x}C] = x * E_g[AC] + (1-x) * E_g[BC] - b * x * (1-x).$$

Solid solutions in two III-V semiconductor series



3 Semiconductor doping

- Substitutional doping
- Intrinsic doping
 - Vacancies
 - Interstitials
- Complexes

3 Substitutional doping

- **Substitutional dopants in Si**

Everything is on a gpIV site

- P_{Si} gpV on a gpIV site
– electron excess –
this is a donor
- B_{Si} gpIII on a gpIV site
– electron deficient –
this is an acceptor

- **Substitutional doping in III-V compounds** – such as InP

e.g. Cd_{In} gpII on a gpIII site – electron deficient = acceptor

e.g. S_P – gpVI on a gpV site = donor

C could occupy the gpIII or the gpV site –
amphoteric dopant

3 Substitutional doping

....cont

- **Substitutional doping in II-VI compounds** – such as CdTe
- On the gpII site...
e.g. Cu_{Cd} gpIA on a gpII site – electron deficient = acceptor
e.g. In_{Cd} – gpIII on a gpII site = donor

- **Substitutional doping in II-VI compounds** – such as CdTe
- On the gpVI site...
e.g. As_{Te} gpV on a gpVI site – electron deficient = acceptor
e.g. Cl_{Te} – gpVII on a gpVI site = donor

3 Native defect or 'intrinsic defect' doping - vacancies

- **Metal i.e. cation vacancies**

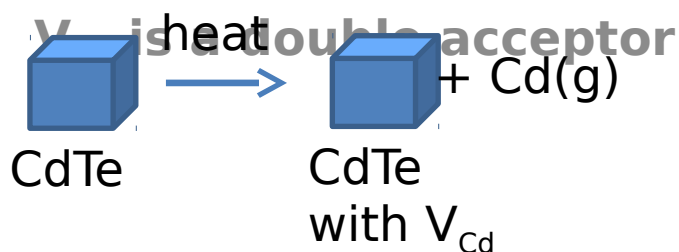
e.g. Cd vacancies in CdTe

Cd oxidation state 2+

Te oxidation state 2-

If you heat CdTe it loses Cd
when neutral Cd leaves it
takes two electrons with it
leaving a doubly +ve charged

V_{Cd}



- **Non-metal i.e. anion vacancies**

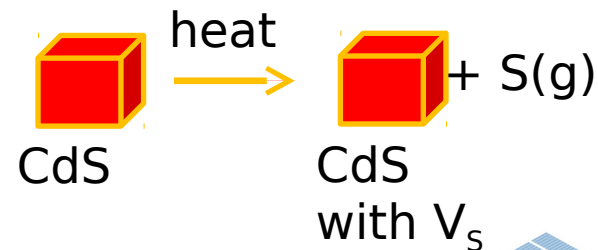
e.g. S vacancies in CdS

Cd oxidation state 2+

S oxidation state 2-

If you heat CdS it loses S
when neutral S leaves it takes
two electrons with it leaving a
doubly -ve charged V_S

V_S is a double donor



3 Native defect or 'intrinsic defect' doping - interstitials

- **Metal i.e. cation interstitials**

e.g. Cd interstitials in CdTe

Cd oxidation state 2+

Te oxidation state 2-

Add neutral Cd to CdTe as an interstitial – to achieve its usual oxidation state it must lose two electrons.

Cd_i is assumed to be a donor

- **Non-metal i.e. anion vacancies**

e.g. Te interstitials in CdTe

Add neutral Te to CdTe as an interstitial – to achieve its usual oxidation state it must gain two electrons.

Te_i is assumed to be a donor

3 Complex centres

- e.g. the 'A-centre'

Add neutral Cd to CdTe
as an interstitial – to
achieve its usual
oxidation state it must
lose two electrons.

Cd_{Te} ' single donor

V_{Cd} •• double acceptor

$[\text{V}_{\text{Cd}} - \text{ClTe}]$ • single
acceptor

This is the 'A-centre'

3 Energy levels in the gap of silicon

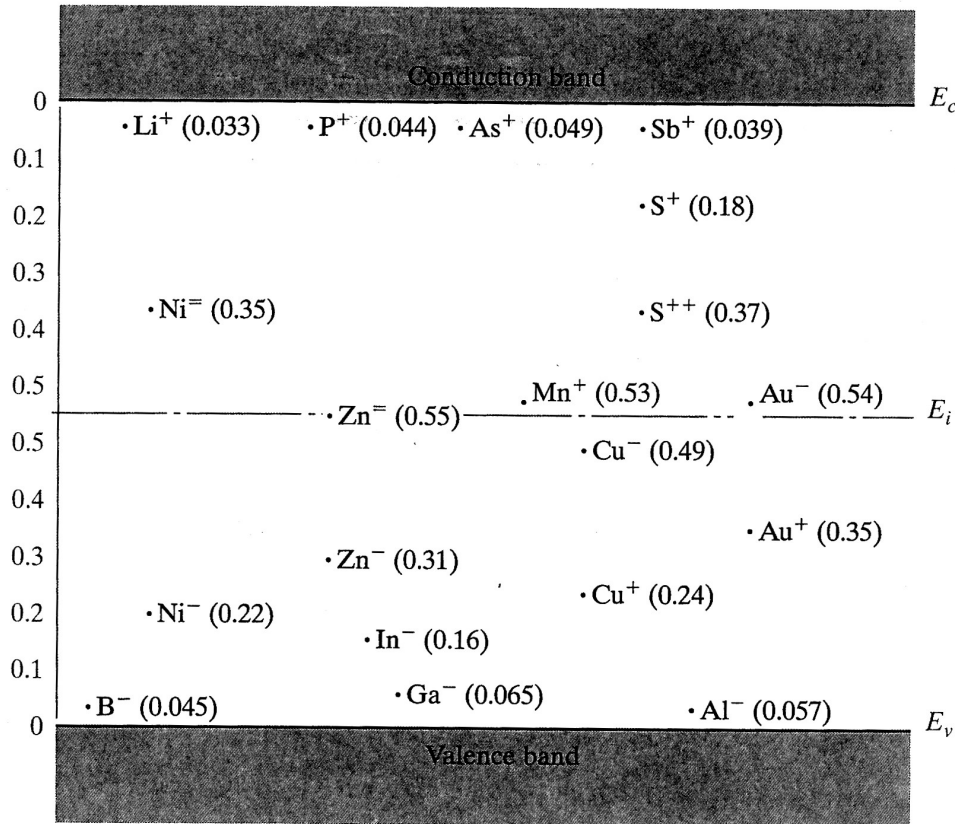


Diagram from Solid State Electronic Devices,
Streetman and Banerjee

3 Kroger – Vink nomenclature for point defects

Examples [\[edit\]](#)

$\text{Al}_{\text{Al}}^{\times}$ = an aluminum ion sitting on an aluminum lattice site, with neutral charge.

$\text{Ni}_{\text{Cu}}^{\times}$ = a nickel ion sitting on a copper lattice site, with neutral charge.

V_{Cl}^{\bullet} = a chlorine **vacancy**, with singular positive charge.

$\text{Ca}_i^{\bullet\bullet}$ = a calcium interstitial ion, with double positive charge.

Cl_i' = a chlorine anion on an interstitial site, with singular negative charge.

O_i'' = an oxygen anion on an interstitial site, with double negative charge.

e' = an electron. A site isn't normally specified.

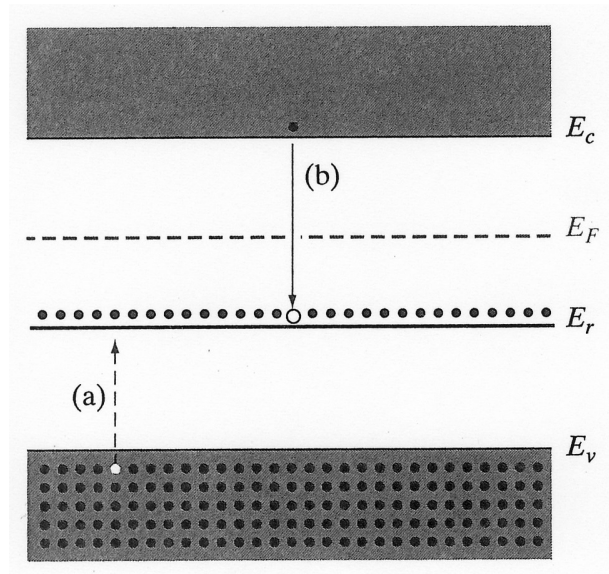
If you need to get specific about point defects and their reactions and equilibria, then check out **Kroger-Vink** nomenclature...

http://en.wikipedia.org/wiki/Kroger-Vink_notation

4 Generation and recombination

- Trapping
- Recombination
- Direct and indirect
- Kinetics for recombination in direct gap materials
- Recombination via trap states ('Shockley Hall Reed' mechanism)

4.1 Trapping centres



- Centres below the Fermi level at E_r are full of electrons.
- For them to act as 'traps', either
 - holes are temporarily trapped there then re-emitted *or*
 - electrons are temporarily trapped there then re-emitted

Diagram from Solid State Electronic Devices,
Streetman and Banerjee

NB strictly this is what 'trapping' is. However the term 'trap' is used more widely than this - as follows now...

4.2.1 Recombination types

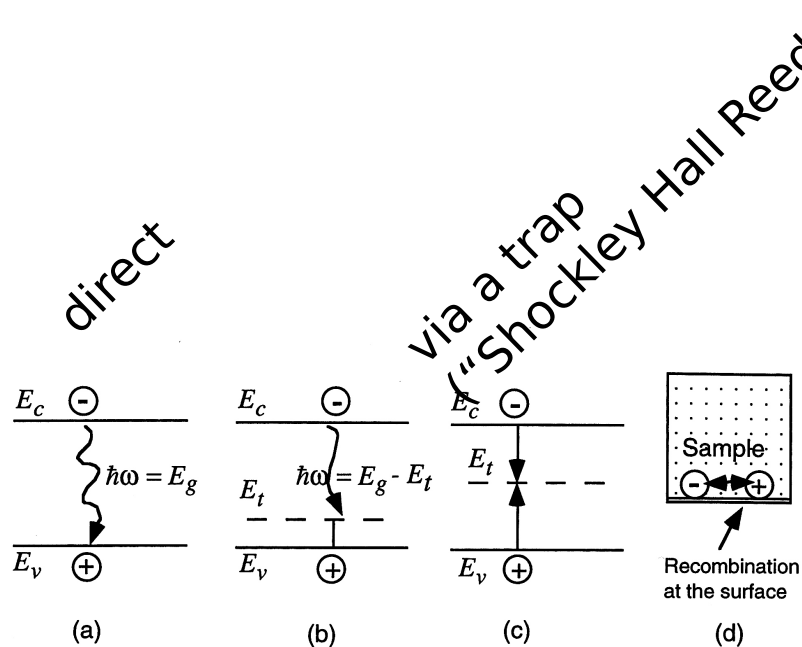


Fig. 3.8.4. (a) Direct (band-to-band) radiative recombination, (b) radiative band-to-impurity recombination, (c) nonradiative recombination via impurity (trap) levels, and (d) surface recombination.

Direct recombination
(a)

It is radiative

Indirect recombination

(b-d) is not usually radiative.

(Auger recombination not shown is also 'indirect')

4.2.2 Kinetics of direct recombination

Symbols

G = generation rate

R = recombination rate

n = negative carriers

p = positive carriers

n_i = intrinsic carrier concentration

$\bar{G}, \bar{R}, \bar{n}, \bar{p}$ - equilibrium values

$\hat{G}, \hat{R}, \hat{n}, \hat{p}$ - excess values under steady state excitation

G, R, n, p - total values

$$G = \bar{G} + \hat{G} \text{ m}^{-3}\text{s}^{-1}$$

$$R = \bar{R} + \hat{R} \text{ m}^{-3}\text{s}^{-1}$$

$$p = \bar{p} + \hat{p} \text{ m}^{-3}$$

$$n = \bar{n} + \hat{n} \text{ m}^{-3}$$

r = rate constant for recombination m^3s^{-1}

• At equilibrium

$$\bar{G} = \bar{R}$$

• Under steady state conditions

(e.g. under illumination), there is

additional generation:

$$G = \bar{G} + \hat{G} \text{ m}^{-3}\text{s}^{-1}$$

4.2.2 Kinetics of direct recombination

Generally: $R = rpn \text{ m}^{-3}\text{s}^{-1}$

For the case where there is additional generation of

$$\hat{G} \text{ pairs m}^{-3}\text{s}^{-1}$$

the recombination rate is written

$$R = \bar{R} + \hat{R} = r(\bar{p} + \hat{p})(\bar{n} + \hat{n}) \text{ m}^{-3}\text{s}^{-1}$$

This can be simplified by substituting

$$\bar{R} = r\bar{p}\bar{n} \text{ m}^{-3}\text{s}^{-1}$$

$$\hat{n} = \hat{p} \text{ m}^{-3}$$

$$\bar{G} + \hat{G} = \bar{R} + \hat{R} \text{ m}^{-3}\text{s}^{-1}$$

$$\hat{n}^2 + \hat{n}(\bar{p} + \bar{n}) = \frac{\hat{G}}{r} \text{ m}^{-6}$$

4.2.2 Recombination in direct gap semiconductors

Examples

Low level injection

$$\hat{n} \ll \bar{n} \text{ or } \hat{n} \ll \bar{p}$$

the n^2 term can be neglected giving:

$$\hat{n} = \frac{\hat{G}}{r(\bar{p} + \bar{n})} \text{ m}^3$$

a) Low level injection, p-type material where $\bar{p} \gg \bar{n}$

$$\hat{n} = \frac{\hat{G}}{r\bar{p}} \text{ m}^3$$

the carrier densities are

$$p = \bar{p} + \hat{p} \cong \bar{p}$$

$$n = \bar{n} + \hat{n} \cong \hat{n}$$

4.2.2 Recombination in direct gap semiconductors

b) Low level injection, n-type material where $\bar{n} \gg \bar{p}$

$$\hat{n} = \frac{\hat{G}}{r\bar{n}} \text{ m}^3$$

the carrier densities are

$$p = \bar{p} + \hat{p} \cong \hat{p}$$

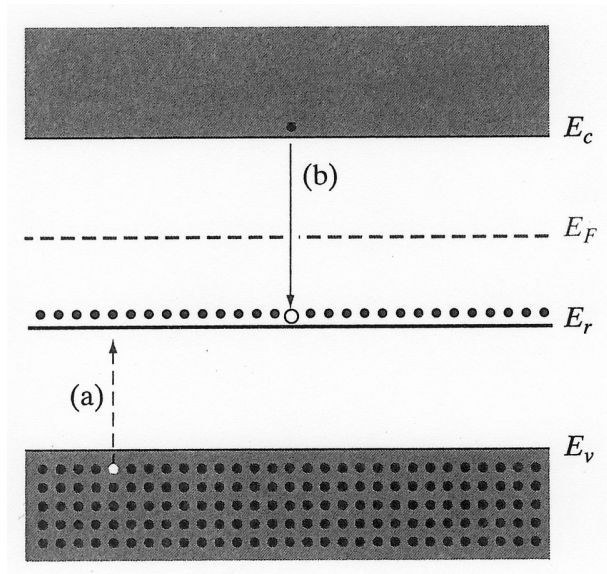
$$n = \bar{n} + \hat{n} \cong \bar{n}$$

Lifetimes

$r\bar{p}$ and $r\bar{n}$ have units s^{-1} they are **lifetimes**

There is a numerical example in M J Cooke, page 69.

4.2.2 Recombination via traps



a) holes are trapped
b) electrons
annihilate with the
trapped holes
overall there is one
electron hole pair
less plus some

*This is most often called
Shockley Hall Read recombination*

4.2.2 Recombination via traps

For the case of recombination via traps (not shown here)

$$R = \frac{np - n_i^2}{\tau_p(n + n_l) + \tau_n(p + p_l)}$$

$$n_l = N_C \exp \frac{(E_t - E_C)}{kT}$$

$$p_l = N_V \exp \frac{(E_V - E_t)}{kT}$$

n_l and p_l are the numbers thermally excited

τ_{pl} and τ_{nl} are the lifetimes

- The recombination rate is maximised when the trap energy E_t is mid-gap.
- These are “killer traps” or “lifetime killers” e.g. Au_{Si}
- Where E_t is mid-gap, the diode factor is $n = 2$

Treatment from Intro to Electronic Devices
M Schur

Example – generation/recombination

■ In one semiconductor material doped p -type with $N_A = 10^{20} \text{ m}^{-3}$ the recombination coefficient is $5 \times 10^{-12} \text{ m}^3 \text{ s}^{-1}$ and $n_i = 10^{16} \text{ m}^{-3}$. Find the minority carrier lifetime, the equilibrium generation rate, and find the electron and hole number densities if light causes an excess generation of $10^{22} \text{ pairs m}^{-3} \text{ s}^{-1}$.

□ The material is p -type with $N_A \gg n_i$, so:

$$\bar{p} \simeq N_A = 10^{20} \text{ m}^{-3}$$

$$\bar{n} \simeq n_i^2 / N_A = 10^{12} \text{ m}^{-3}$$

The minority carrier lifetime (τ_e) is

$$\begin{aligned}\tau_e &= 1/r\hat{p} \\ &= 2 \times 10^{-9} \text{ s}\end{aligned}$$

The equilibrium generation rate \bar{G} is found by:

$$\bar{G} = \bar{R} = r\bar{p}\bar{n}$$

therefore $\bar{G} = 5 \times 10^{20} \text{ m}^{-3} \text{ s}^{-1}$.

Example cont...

Assuming the light causes only low level injection:

$$\begin{aligned}\hat{n} = \hat{p} &= \hat{G}/r\bar{p} \\ &= 2 \times 10^{13} \text{ m}^{-3}\end{aligned}$$

The assumption is verified, because $\hat{n} \ll \bar{p}$.

Hence the number densities can be found:

$$\begin{aligned}n = \bar{n} + \hat{n} &= 10^{12} + 2.10^{13} \\ &= 2.1 \times 10^{13} \text{ m}^{-3} (\simeq \hat{n})\end{aligned}$$

$$\begin{aligned}p = \bar{p} + \hat{p} &= 10^{20} + 2.10^{13} \\ &\simeq 10^{20} \text{ m}^{-3} (= \bar{p})\end{aligned}$$

So low level injection has increased the minority electron number density by a factor of 20, while hardly disturbing the majority hole number density.

(Note that the injection was still low level even though $\hat{G} \gg \bar{G}$ in this case. This is examined further in Exercise 6(b).)

Books used to compile this lecture (including picture credits)

- Semiconductor Devices, M J Cooke
- Intro to Electronic Devices, M Shur
- Solid State Electronic Devices, B G Streetman and S K Banerjee
- Solid State Physics, AK Dekker