ME4252 Nanomaterials for Energy Engineering

Semiconductors continued....

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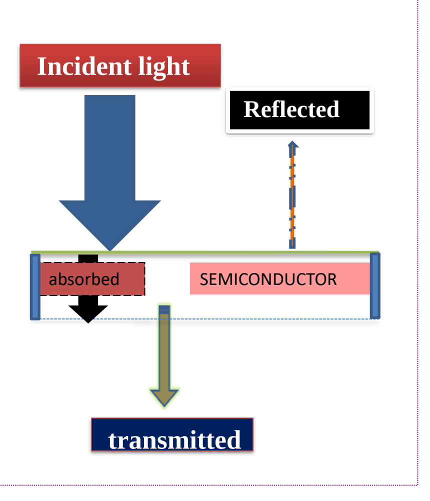
Photon Absorption: Interaction of light with semiconductor

Photons incident on the surface of a semiconductor will be either reflected from the top surface, or will be absorbed in the material or, failing either of the above two processes, will be transmitted through the material.

For photovoltaic devices, reflection and transmission are typically considered loss mechanisms as photons which are not absorbed do not generate power

If the photon is absorbed it will raise an electron from the valence band to the conduction band - photogeneration



Light absorption

Photons falling onto a semiconductor material can be divided into three groups based on their energy compared to that of the semiconductor band gap:

1. $E_{ph} < E_g$

- photons interact only weakly with the semiconductor, passing through it as if it were transparent

2. $E_{ph} = E_g$

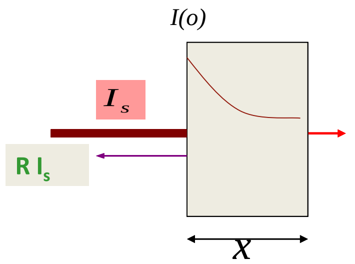
- photons are efficiently absorbed and creates an electron-hole pair

3. $E_{ph} > E_g$

- photons with energy much greater than the band gap are strongly absorbed and creates an electron-hole pair

- the excess energy will be dissipated as heat creating phonons in the semiconductor

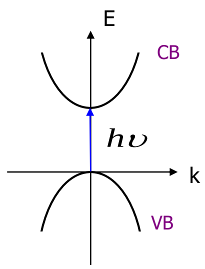
Absorption Coefficient

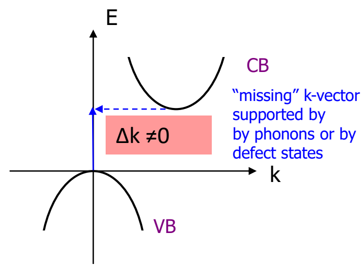


$$I(x) = (1-R)I_s \exp(-\alpha x)$$
$$= I(0)\exp(-\alpha x)$$

Fig shows the attenuation of light intensity in a crystal slab of absorption α and thickness, *x*. A fraction, **R** of the light from the sun, I_s , is reflected at the front surface. The remaining intensity attenuates exponentially with distance in a uniform material, as shown by curved black line. I(0) is the intensity just inside the surface (i.e. after accounting for reflection)

Energy and momentum conservation:
Direct & indirect semiconductors





Direct bandgap

Efficient light - matter interaction

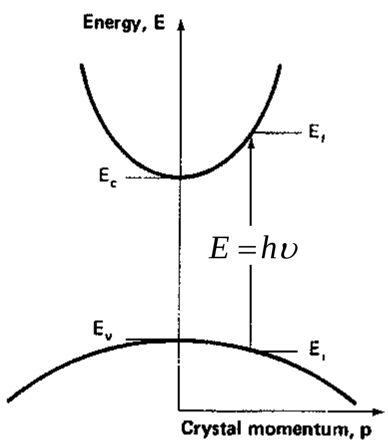
Indirect bandgap

inefficient light –matter interaction

Phonons are quanta of lattice vibrations with typical energy per phonon in the range 0.01 *eV* - 0.1 *eV, less energy than photons but with relatively high momentum.*

Direct transition

- **Occurs in *direct band gap* material such as GaAs**
- A photon (a "particle of light") with energy $E = h\upsilon$, can be absorbed by promoting a valence band electron to the conduction band, creating an electron-hole pair
- Direct bandgap materials have strong light absorption



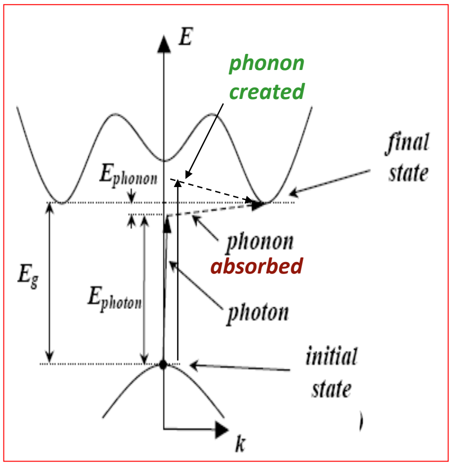
Indirect transition

Energy conservation:

phonon absorbed

$$E_g = E_f - E_i = E_{photon} \pm E_{phonon}$$

phonon created



Momentum conservation:

$$\vec{k_f} - \vec{k_i} = \vec{k}_{photon} \pm \vec{k}_{phonon}$$

Absorption coefficient vs. wavelength

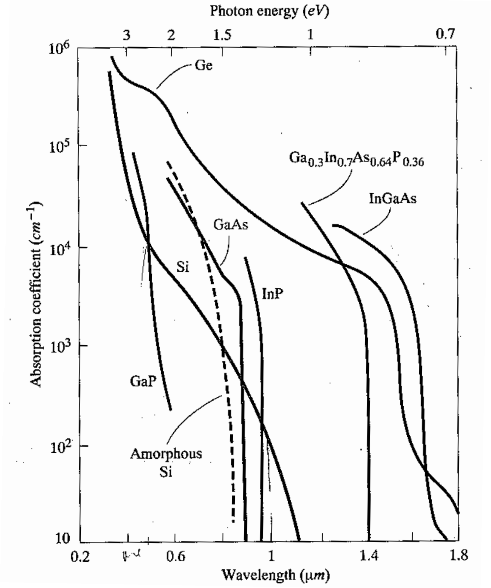


Figure: **Absorption coefficient as a function of wavelength for several direct bandgap and indirect bandgap semiconductors**

Recombination

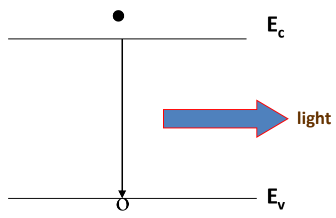
- Recombination is part of a process to restore equilibrium of a semiconductor that has been perturbed, or disturbed out of equilibrium.
- A typical recombination reaction requires one electron and one hole
- Recombination occurs when there is an excess of carriers and they are destroyed, by recombining. For example, the concentration of carriers in illuminated materials will be in excess of their values in dark. If light is switched off, these concentrations decay back to the equilibrium values. Process by which this decay occurs is known as recombination
- When they are destroyed, a negatively charged electron is attracted to a positively charged hole, and as they get together, their charges are canceled and the electron is part of a bond once again.
- There are several recombination mechanisms that occurs in a photovoltaic device

Types of Recombination

1. Band-to-band recombination
2. SRH recombination
3. Auger recombination
4. Surface recombination

Band to Band (Radiative) Recombination

- It is also referred as "Direct recombination"
- It is the direct annihilation of a conduction band electron and a valence band hole
- The electron falls from an allowed conduction band state into a vacant valence band state



Band to band recombination

- **The energy released during this process usually produces a photon and emits light (LED)**
  - **This is often known as radiative recombination, and also called spontaneous emission**

Band to Band (radiative and non-radiative) Recombination

Direct band gap :

- In a direct band gap semiconductor, electrons at the conduction-band minimum can recombine directly with holes at the valence band maximum, while conserving momentum
- The energy of the recombination across the band gap will be emitted in the form of a photon of light.

Indirect band gap :

- Recombination occurs with the mediation of a third body, such as a phonon or a crystallographic defect, which allows conservation of momentum
- Often release the band gap energy as phonons, instead of photons, and thus do not emit light significantly
- Light emission from indirect semiconductors is very inefficient and weak

SRH recombination

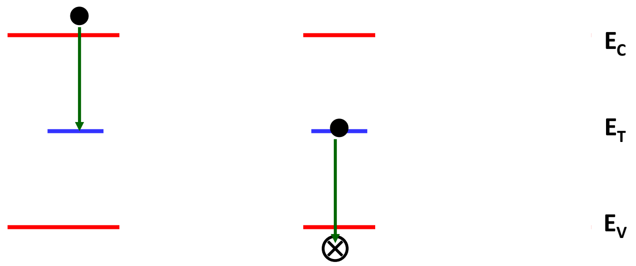
- A defect or impurity in the material often causes an energy state in the band gap that can act as traps for carriers. These defect levels create a very efficient two-step recombination process whereby electrons relax from CB energies to defect levels and then relax to the VB annihilating a hole.
- This type of recombination is termed as **Shockley-Read-Hall** recombination or SRH recombination
- This type of recombination does not take place in perfectly pure and non-defective material

- SRH recombination is a two step process:

1. An electron (or hole) is trapped by an energy state in the forbidden region.

2. If a hole (or an electron) moves up to the same energy state before the electron is thermally reemitted into the conduction band, then it recombines

Possible electronic transitions between a trap level and the energy bands

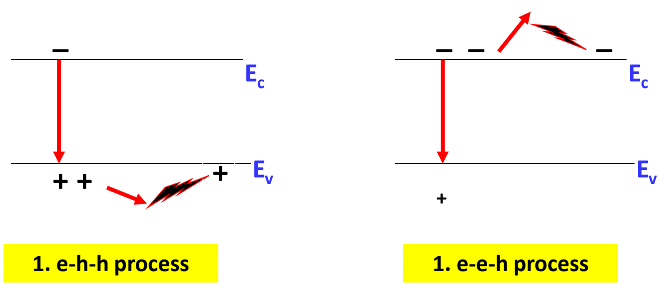


SRH non-radiative recombination

SRH recombination

- This process is typically non-radiative i.e. releases thermal energy or produces lattice vibrations
- The rate at which a carrier moves into the energy level in the forbidden gap depends on the distance of the introduced energy level from either of the band edges.
- If an energy level is introduced close to either band edge, recombination is less likely as the electron is likely to be re-emitted to the conduction band edge rather than recombine with a hole which moves into the same energy state from the valence band.
- The energy levels near mid-gap are very effective for recombination
- This indirect recombination is very likely in the indirect band gap semiconductors

Auger Recombination



- It is a type of band-to-band recombination that involves three particles
- In Auger recombination, extra energy released by the recombination of an electron-hole pair is transferred (instead of emitting light) to third free carrier (electron in CB or hole in VB) which is raised in energy deep onto the respective band.
- In other words, one carrier loses energy and the other gains it. The one that loses it is recombined, and the one that gains it goes to a higher energy level

Auger Recombination

- Eventually, this highly energized carrier "thermalizes" - loses energy in small steps through heat producing collisions with the semiconductor lattice, until it eventually recombines or gains energy once more

- It's a non-radiative recombination process

- Auger recombination is effective when the carrier concentration is high, especially in low band gap and doped semiconductors (impurity levels greater than 10^{17} /cm^3), or at high temperatures

Auger recombination can also occurs via traps:

- The collision of an electron with an occupied trap state close to the conduction band can stimulate the recombination of the electron in the trap state with a valence band hole by gaining the kinetic energy

- Similarly a hole colliding with an empty trap close to the valence band can stimulate recombination of the hole in the trap state with a conduction band electron

17

Similarities & Dissimilarities

Similarities :

- They all annihilate an electron for each hole
- They all produce some kind of energy, whether it be heat or light, in the process

Differences :

- **Band-to-band recombination** only uses the fact that the carriers of opposite charge happen to be in the same vicinity, no outside interference is needed
- *SRH* **recombination** uses energy levels in the band gap to which the carriers can move up or down, closer to their opposite charge so the attraction can destroy them
- **Auger recombination** uses collisions between electrons to transfer energy from one electron to another, sending one to a higher energy and another to a lower one where it is attracted to a hole and they both are annihilated

Carrier Lifetime

- **The minority carrier lifetime is a measure of how long a carrier is likely to stay around before recombining.**
- **It is often just referred to as the "lifetime" and has nothing to do with the stability of the material.**
- **Usually, minority carrier lifetime is given by:**

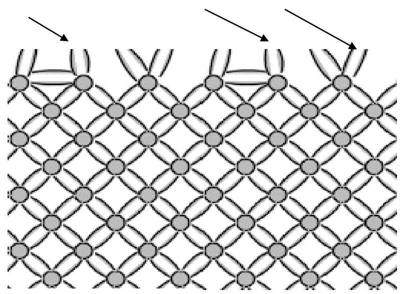
$$\frac{1}{\tau_{bulk}} = \frac{1}{\tau_{Band}} + \frac{1}{\tau_{Auger}} + \frac{1}{\tau_{SRH}}$$

???

Surface Recombination

- Localized states within or at the surface of the semiconductor or interfaces promote recombination
- Surfaces and interfaces typically contain a large number of recombination centers because of the abrupt termination of the semiconductor crystal, presence of extrinsic impurities etc.
- In addition, the surfaces and interfaces are more likely to contain impurities since they are exposed during the device fabrication process
- Recombination at surfaces and interfaces does have a significant impact on the behavior of photovoltaic devices
- Surface recombination can be controlled

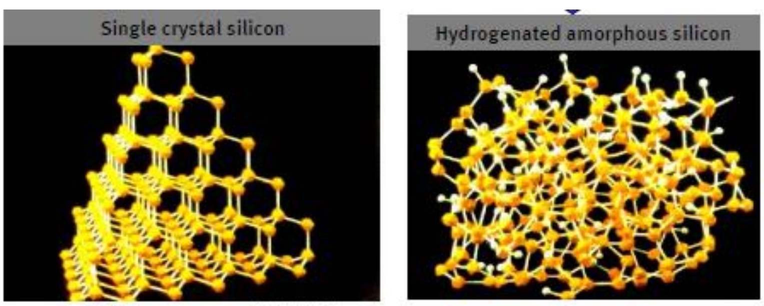
Reason: Dangling bonds at the surface of the semiconductor

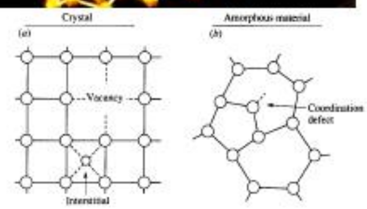


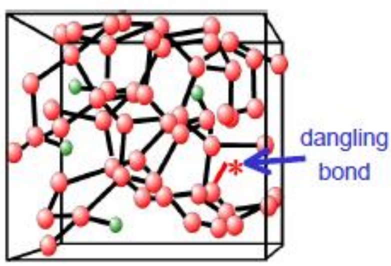
Dangling bonds at the surface

- **The defects at a semiconductor surface are caused by the interruption to the periodicity of the crystal lattice, which causes dangling bonds at the semiconductor surface**

Differences in the type of defects present







Defect in a crystal: atom dislocation
Defect in amorphous silicon: coordination defects

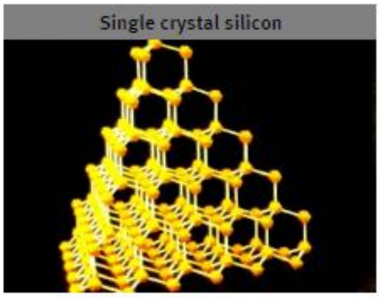
Why to avoid this?

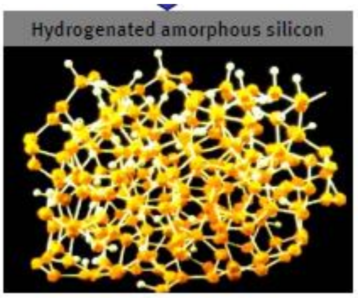
- **Reduction of the number of dangling bonds,**
- **This takes care in the reduction of the recombination**

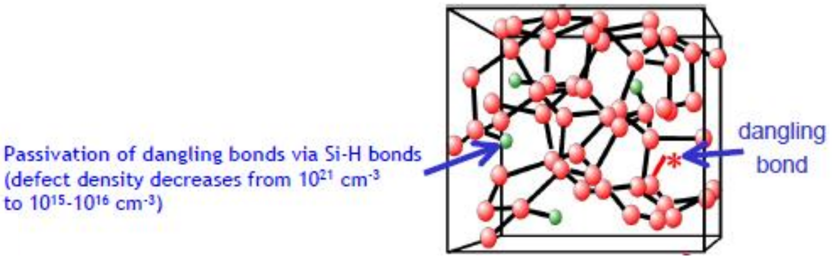
How to achieve this ?

- **It can be achieved by growing a layer on top of the semiconductor surface which ties up some of these dangling bonds**
- **This reduction of dangling bonds in known as surface passivation**

a-Si:H dangling bonds







a-Si:H dangling bonds

Example for Passivation :

- **Termination of bonds on the semiconductor surface with elements assuring chemical stability of the surface;**
- **Surface is now chemically "passive"**
- **For example - hydrogen termination of bonds on the silicon surface will prevent oxidation of the surface; oxidation of Si surface bonds will also passivate the surface.**

How it happens?

- **The broken silicon bonds on the surface are saturated with hydrogen**
- **Si-H is a stable bond preventing oxidation of silicon at room temperature**