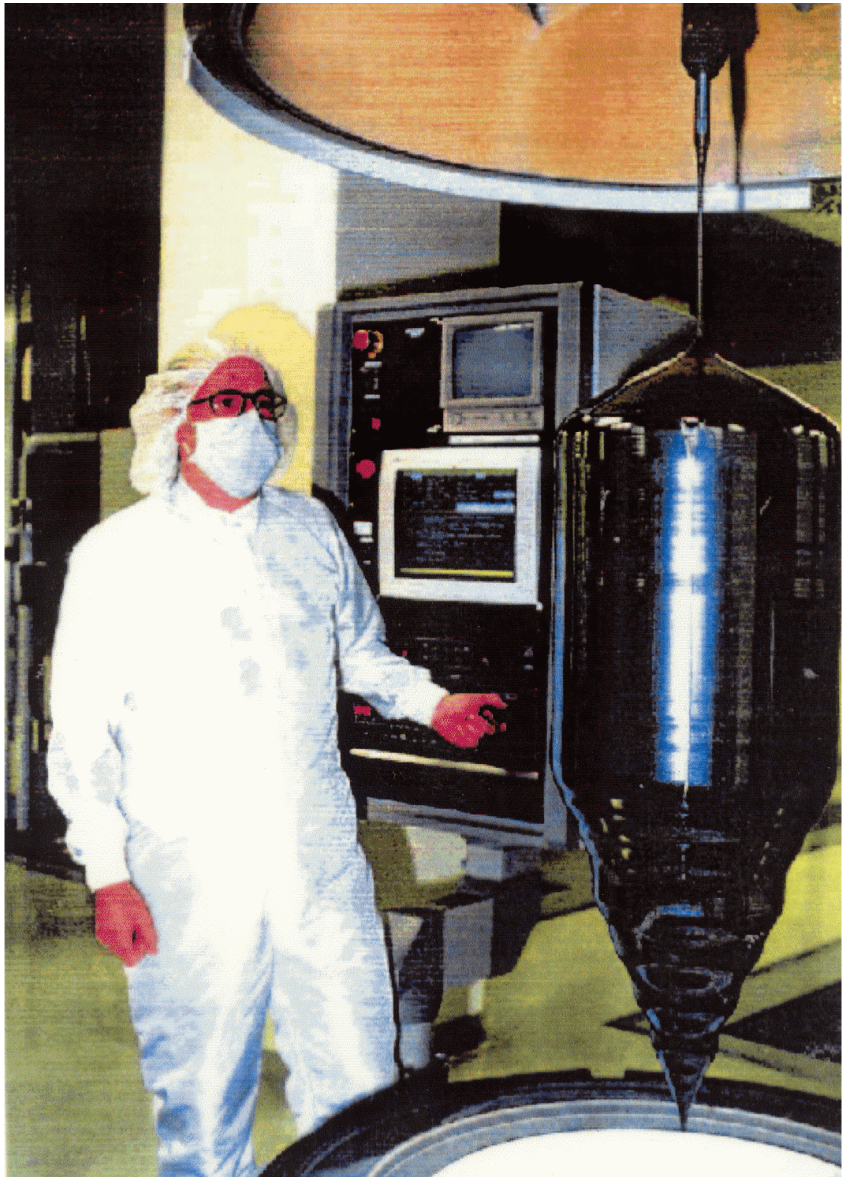
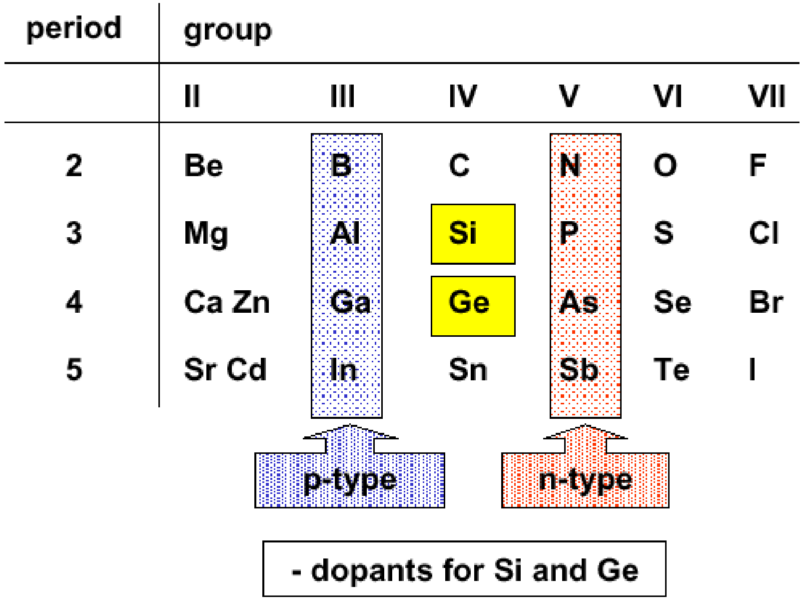


Semiconductor crystals

- Overview
- The concept of hole and effective mass
- Intrinsic semiconductor
- Doped semiconductor

Family of semiconductor

- Elements



period	group					
	II	III	IV	V	VI	VII
2	Be	B	C	N	O	F
3	Mg	Al	Si	P	S	Cl
4	Ca Zn	Ga	Ge	As	Se	Br
5	Sr Cd	In	Sn	Sb	Te	I

p-type

n-type

- dopants for Si and Ge

- Compounds

IV - IV bonding	III - V bonding	II - VI bonding
C SiC Si GeSi Ge Sn	AlP AlAs, GaP AlSb, GaAs, InP GaSb ,InAs InSb	ZnS ZnSe, CdS ZnTe, CdSe, HgS CdTe, HgSe HgTe

Bonding becomes more ionic

Basic properties

(at 300K)	Ge	Si	GaAs	GaN
energy gap (eV)	0.67 (i)	1.11 (i)	1.43 (d)	3.39 (d)
lattice type	Diamond	Diamond	Zincblend	Wurtzite

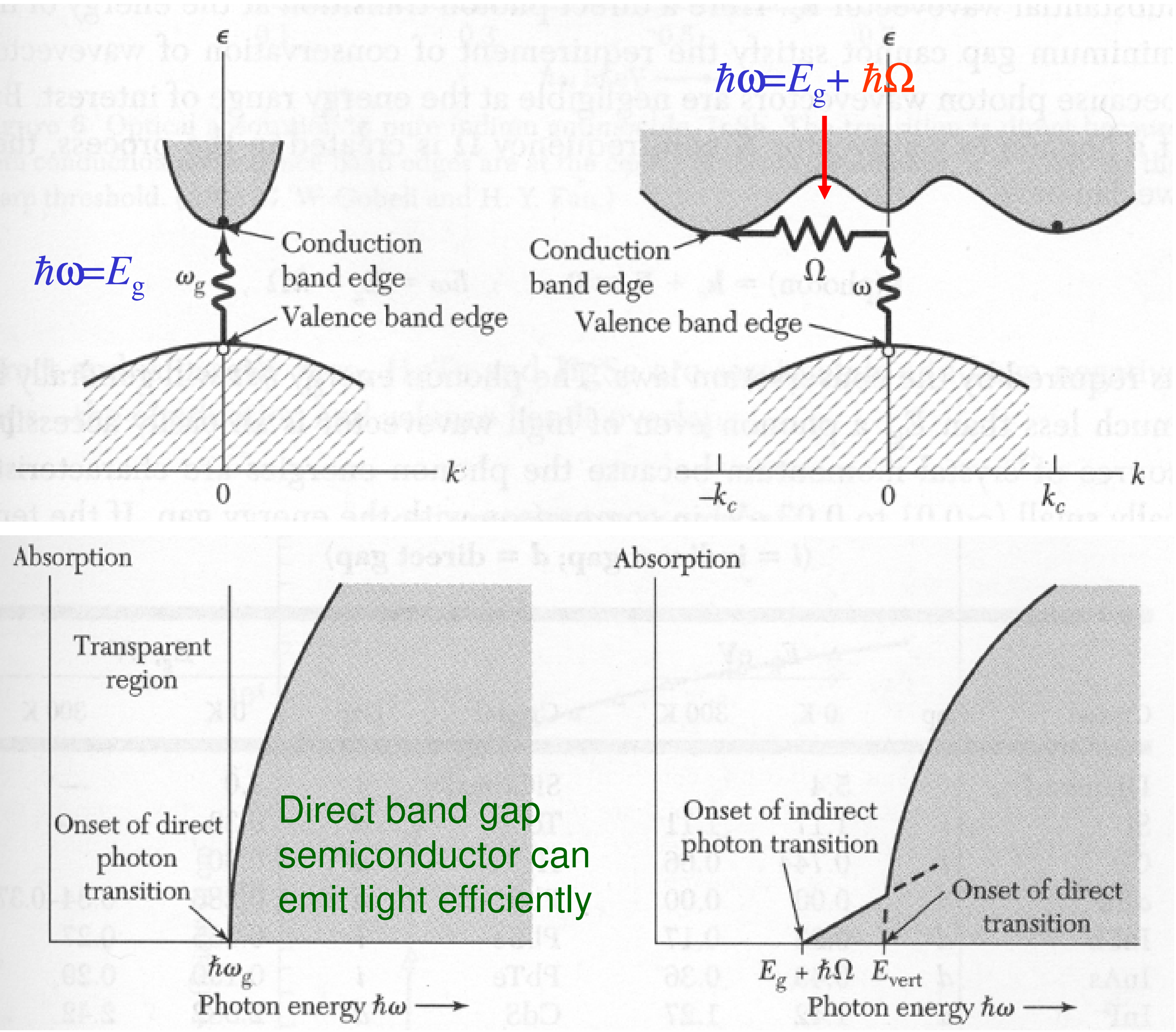
2 overlapping hcp lattices

- Semiconductor is insulator at 0 K, but because of its smaller energy gap (insulator diamond = 5.4 eV), electrons can be thermally excited to the conduction band (and transport current).

- Si-based device can endure higher working temperature than Ge-based (75 ^{o}C) device (∵ Si has a larger band gap).

For some interesting history of semiconductor industry, see 矽晶之火, by M.Riordan and L.Hoddeson.

- Direct band gap (GaAs, GaN…)
- Indirect band gap (Si, Ge…)



Direct band gap semiconductor can emit light efficiently

(1 μm=1.24 eV)

- Overview
- The concept of hole and effective mass
- Intrinsic semiconductor (no doping)
- Doped semiconductor

A filled band does not carry current (Peierls, 1929)

- Electric current density

$$\vec{j}=\frac{1}{V}\sum_{\text{filled }\vec{k}}(-e\vec{v})=-e\int\frac{d^3k}{(2\pi)^3}\frac{1}{\hbar}\frac{\partial\varepsilon_n(\vec{k})}{\partial\vec{k}}$$

- Bravais lattice has inversion symmetry,

$\varepsilon_n(k)=\varepsilon_n(-k)$

→ electrons with momenta *ħk* and -*ħk* have opposite velocities

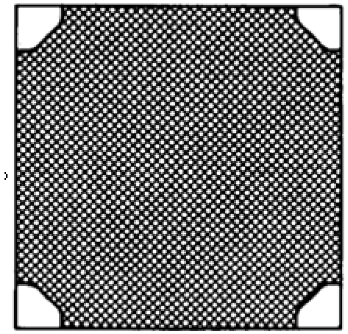
→ no net current in equilibrium

A nearly-filled band

$$\vec{j}=-\frac{e}{V}\sum_{\text{filled }\vec{k}}\vec{v}$$

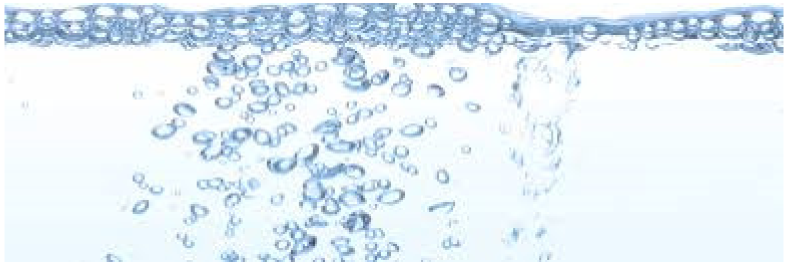
$$=-\frac{e}{V}\left(\sum_{\vec{k}\in\text{1st BZ}}\vec{v}-\sum_{\text{unfilled }\vec{k}}\vec{v}\right)$$

$$=+\frac{e}{V}\sum_{\text{unfilled }\vec{k}}\vec{v}$$



∴ unoccupied states behave as +e charge carriers

The concept of hole (Peierls, 1929)



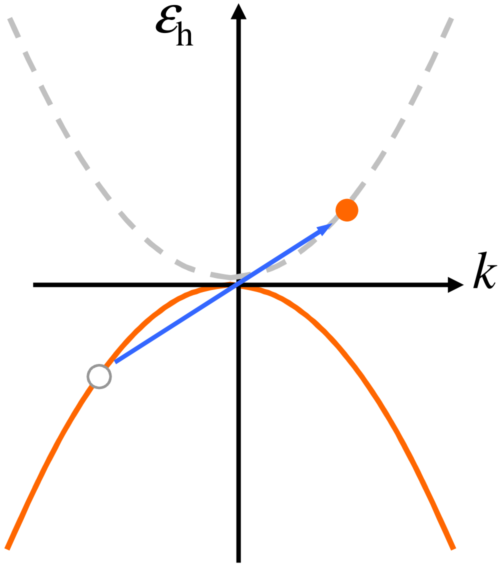
- If one electron of wavevector k_e is missing, then $\sum k = -k_e$. That is, a hole with wavevector k_h is produced (and $k_h = -k_e$).

- The lower in energy the missing electron lies, the higher the energy of the whole system. If the energy of a filled valence band is set to zero, then

$$E_{\text{one band}} = \sum_{\text{filled band}} \varepsilon_e(\vec{k}) - \varepsilon_e(\vec{k}_0)$$

$$= -\varepsilon_e(\vec{k}_0) \equiv \varepsilon_h(-\vec{k}_0)$$

The missing electron

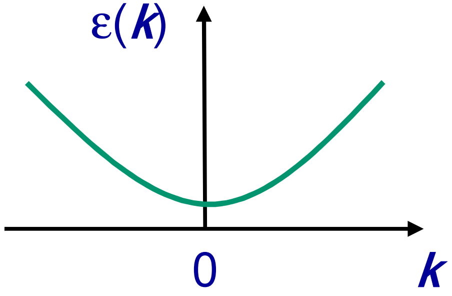


important

Effective mass

Near the bottom of a conduction band, the energy dispersion is approximately parabolic,

$$\varepsilon(\vec{k}) = \varepsilon_0 + \frac{1}{2}\sum_{i,j}\frac{\partial^2\varepsilon(\vec{k})}{\partial k_i \partial k_j}k_i k_j + O(k^3) \approx \varepsilon_0 + \frac{1}{2}\sum_{i,j}\left(\frac{1}{m^*}\right)_{ij} p_i p_j$$



Effective mass matrix $\left(\frac{1}{m^*}\right)_{ij} \equiv \frac{1}{\hbar^2}\frac{\partial^2\varepsilon(\vec{k})}{\partial k_i \partial k_j}$

The electron near band bottom is like a free electron (with m*).

- For a spherical FS, $m^*_{ij}=m^*\delta_{ij}$, only one m* is enough.
- In general, electron in a flatter band has a larger m*.

Negative effective mass

If ε(*k*) is ∩ (e.g. top of valence band), then $m^* < 0$

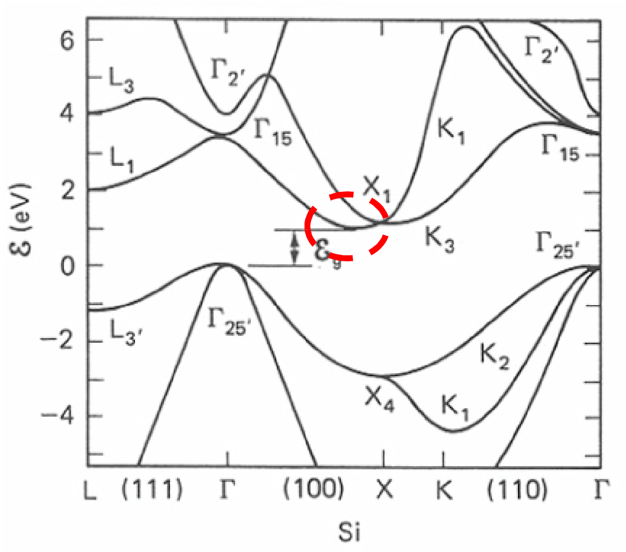
$$a_i = \frac{d}{dt} \upsilon_{gi} = \frac{d}{dt}\frac{d\omega}{dk_i} = \sum_j \frac{d^2\omega}{dk_i dk_j} \dot{k}_j = \sum_i (m^{*-1})_{ij} \hbar \dot{k}_j$$

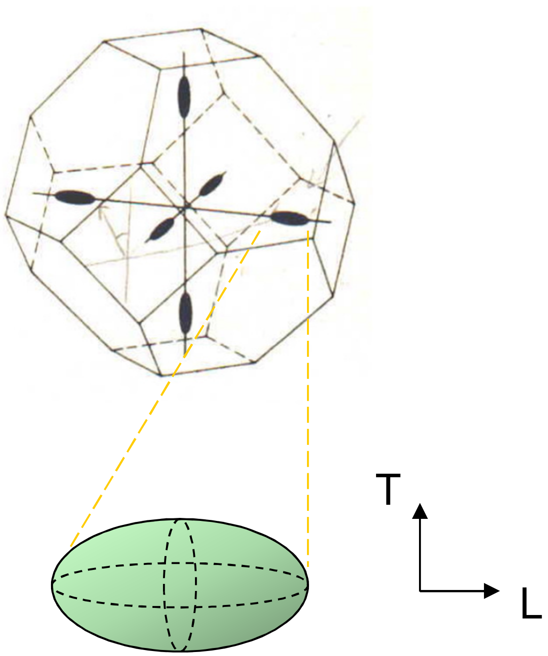
$$\text{or} \quad \overleftrightarrow{m}^* \vec{a} = \hbar \dot{\vec{k}} = -e\vec{E}$$

∴ electron (-e) with negative m_e^*
= hole (+e) with positive m_h^* (=– m_e^*).

For ellipsoidal FS, there can be at most three different m^*s

Eg. the FS of Si is made of six identical ellipsoidal pockets.





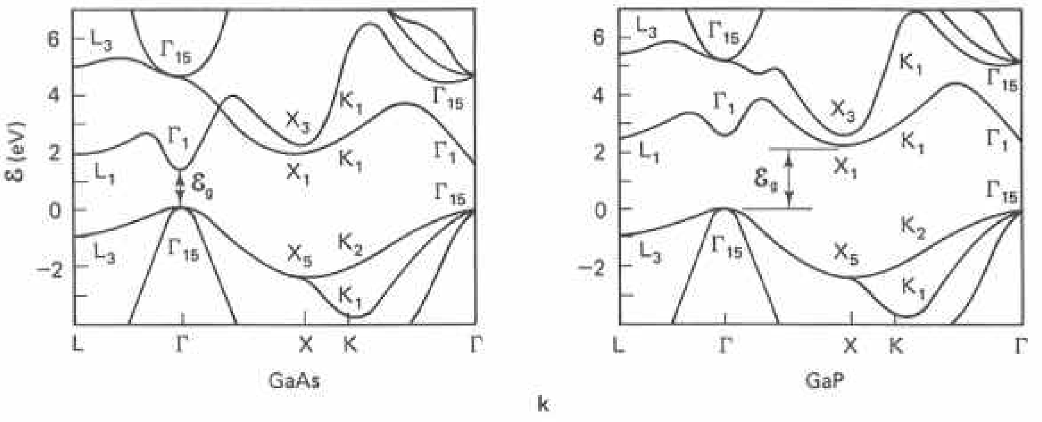
$$\varepsilon(\vec{k}) = \varepsilon_g + \frac{\hbar^2 k_x^{\ 2}}{2m_L} + \frac{\hbar^2 k_y^{\ 2}}{2m_T} + \frac{\hbar^2 k_z^{\ 2}}{2m_T}$$

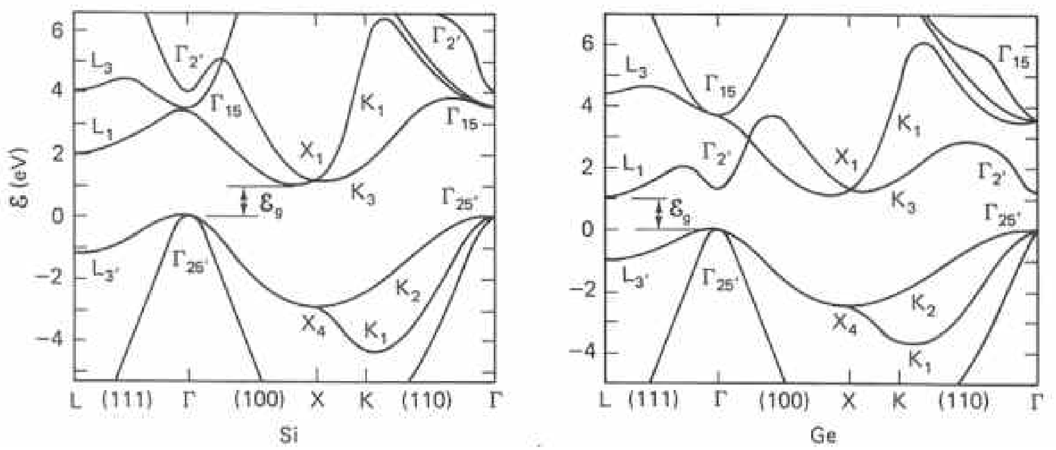
For Si, $\varepsilon_g = 1.1$ eV, $m_L = 0.9\ m$, $m_T = 0.2\ m$

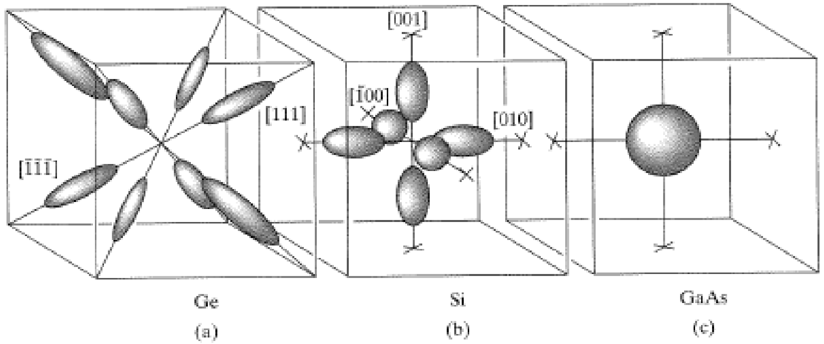
It’s more difficult for the electron to move along L (for one pocket).

The mass is larger because the band is flatter along that direction.)

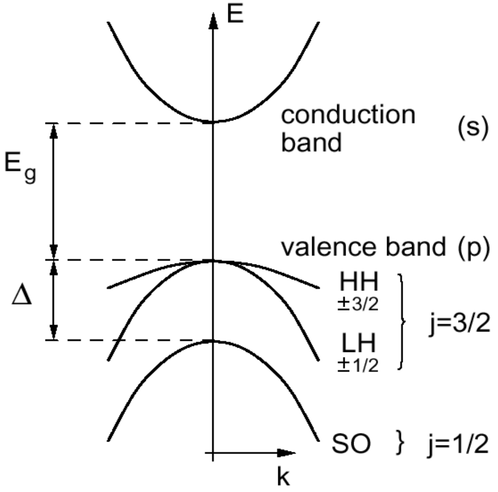
More band structures and Fermi surfaces







Common features



Some useful parameters

	m_L/m_T	m_{HH}/m_{LH}	Δ
Si	0.91/0.19	0.46/0.16	0.044 eV
GaAs	0.063	0.5/0.076	0.3 eV

- Overview
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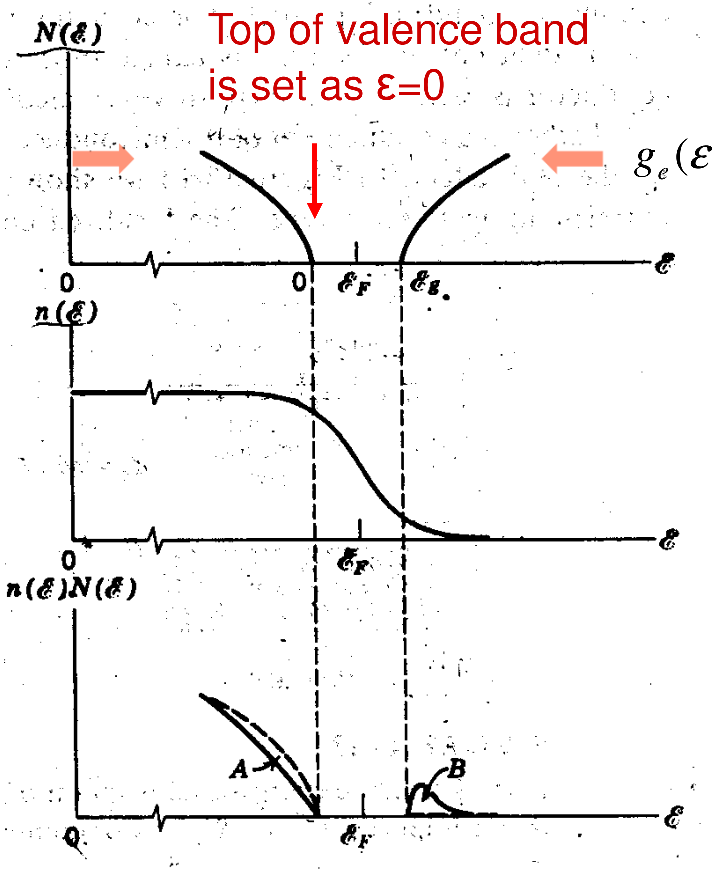
- Doped semiconductor

DOS and carrier density

- DOS for free electron (ch 6) $D(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}$
- DOS (per volume) for semiconductor

$$g_h(\varepsilon) = \frac{1}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2}\sqrt{-\varepsilon}$$



Top of valence band is set as ε=0

$$g_e(\varepsilon) = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon-\varepsilon_g}$$

- Fermi distribution

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)k_BT}+1}$$

$$(\mu = \frac{\varepsilon_g}{2} \quad \text{if} \quad m_e = m_h)$$

- carrier density

$$n = \int_0^\infty f(\varepsilon)g(\varepsilon)d\varepsilon$$

HW: Show that for ellipsoidal FS,

$$m_e^3 = m_1^* m_2^* m_3^*$$

Density of intrinsic carriers

For electrons $f_e(\varepsilon) = \dfrac{1}{e^{(\varepsilon-\mu)k_BT}+1}$

ε-μ >> $k_B T$, $f_e(\varepsilon) \approx e^{-(\varepsilon-\mu)/k_BT} \ll 1$

- electron density in conduction band:

$$n_i = \int_{\varepsilon_g}^{\infty} f_e(\varepsilon) g_e(\varepsilon) d\varepsilon$$

$$\approx \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} \int_{\varepsilon_g}^{\infty} (\varepsilon-\varepsilon_g)^{1/2} e^{(\mu-\varepsilon)/k_BT} d\varepsilon$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} e^{(\mu-\varepsilon_g)/k_BT}$$

$$\times \underbrace{\int_0^{\infty} (\varepsilon-\varepsilon_g)^{1/2} e^{-(\varepsilon-\varepsilon_g)/k_BT} d(\varepsilon-\varepsilon_g)}_{=\sqrt{\pi}/2}$$

$$= N_C e^{(\mu-\varepsilon_g)/k_BT}$$

$$N_C = 2\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2}$$

$$= 2.5\left(\frac{m_e}{m}\right)^{3/2}\left(\frac{T}{300\,\mathrm{K}}\right)^{3/2} \times 10^{19}\,/\,\mathrm{cm}^3$$

For holes $f_h(\varepsilon) \equiv 1 - f_e(\varepsilon) = \dfrac{1}{e^{(\mu-\varepsilon)k_BT}+1}$

μ- ε>> $k_B T$, $f_h(\varepsilon) \approx e^{(\varepsilon-\mu)/k_BT} \ll 1$

- hole density in valence band:

$$p_i = \int_{-\infty}^{0} [1 - f_e(\varepsilon)] g_h(\varepsilon) d\varepsilon$$

$$\approx \frac{1}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2} \int_{-\infty}^{0} (-\varepsilon)^{1/2} e^{(\varepsilon-\mu)/k_BT} d\varepsilon$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2} e^{-\mu/k_BT} \int_0^{\infty} \varepsilon^{1/2} e^{-\varepsilon/k_BT} d\varepsilon$$

$$= N_V e^{-\mu/k_BT}$$

$$N_V = 2\left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2}$$

$$\boxed{n_i p_i = \underbrace{N_C N_V}_{\sim T^3} e^{-\varepsilon_g/k_BT}}$$

Independent of μ (valid even with doping)

Carrier density and energy gap

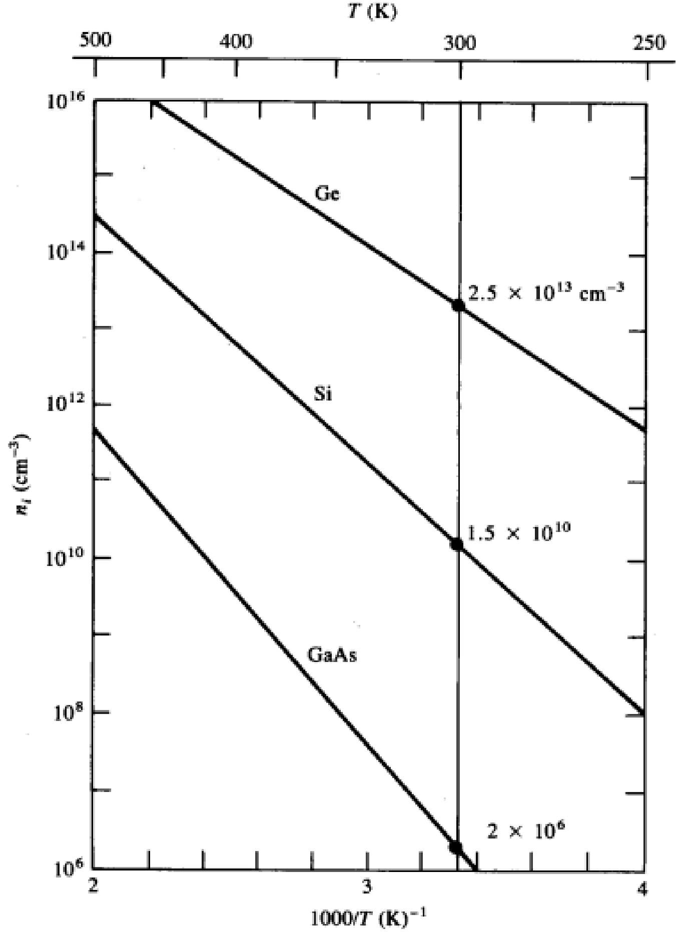
In intrinsic semiconductor,

$$n_i = p_i = (N_C N_V)^{1/2} e^{-E_G/2k_BT}$$

Density of intrinsic carriers depends only ε_g and *T*.

300K	ε_g (eV)	n_i
Ge	0.67	2.4×10^{13}
Si	1.12	1.45×10^{10}
GaAs	1.42	1.79×10^{6}

(For Si, atom density = 5×10^{22}cm^{-3}.)



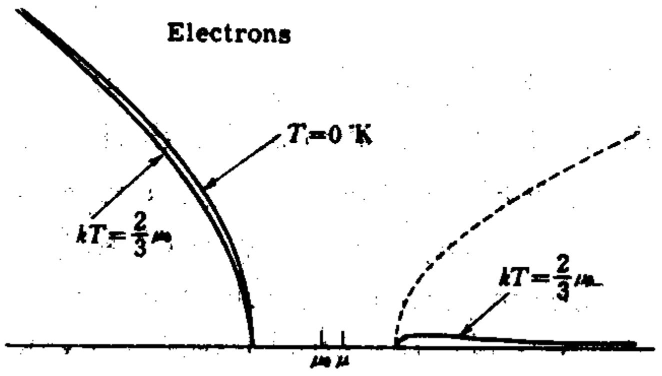
- Position of chemical potential

$$e^{(2\mu - E_G)/k_BT} = N_V / N_C$$

$$\rightarrow \mu = \frac{1}{2}E_G + \frac{1}{2}k_BT\ln(N_V/N_C)$$

$$= \frac{1}{2}E_G + \frac{3}{4}k_BT\ln(m_h/m_e)$$

2nd term very small because $k_BT \ll E_G$



- Overview
- The concept of hole and effective mass
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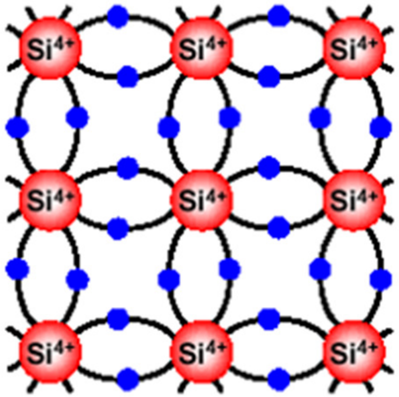
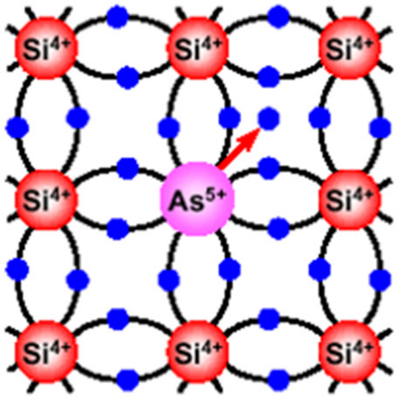
- Doped semiconductor

Extrinsic carriers by doping

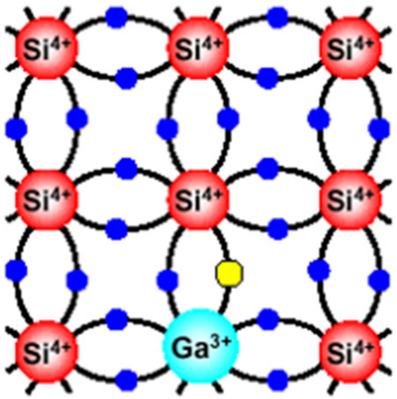
Intrinsic



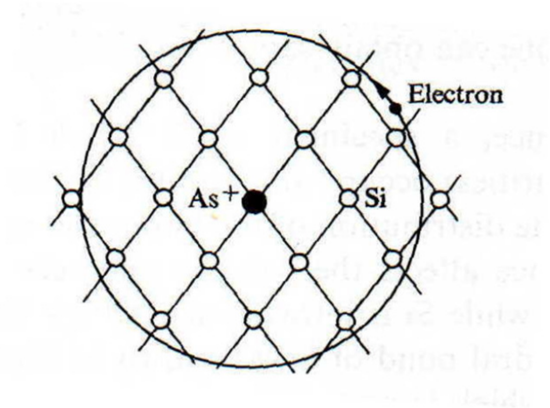
extrinsic (n-type)



extrinsic (p-type)



Bohr model of Impurity level



- Assume an ionized donor atom has a hydrogen-like potential,

(Ref: Eisberg and Resnick, $m \rightarrow m_e$, $\varepsilon_0 \rightarrow \varepsilon$)

$$E_D = \frac{e^4 m_e}{2\varepsilon^2 \hbar^2} = \left(\frac{13.6}{\varepsilon^2} \frac{m_e}{m} \right) \text{eV}$$

Dielectric constant of Si = 11.7 (Ge=15.8, GaAs=13.13),

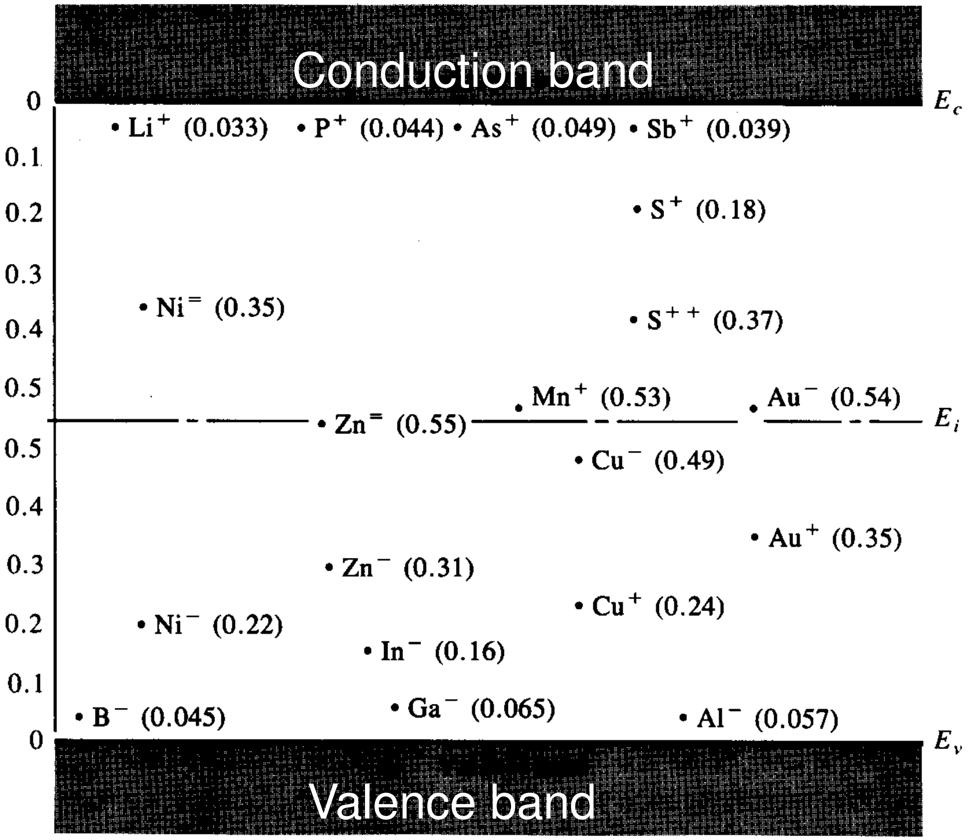
Effective mass for Si = 0.2 m.

- Therefore, the donor ionization energy = 20 meV.
- Bohr radius of the donor electron:

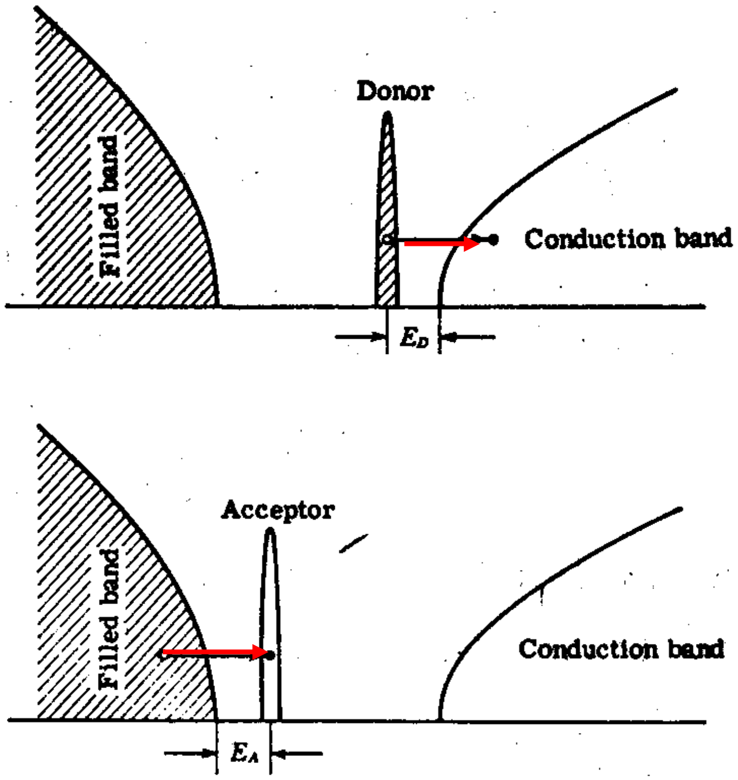
$$a_D = \frac{\varepsilon \hbar^2}{m_e e^2} = \left(\frac{0.53\varepsilon}{m_e / m} \right) \text{A}$$

For Si, it's about 50 A (justifies the use of an effective ε).

- Impurity levels in Si

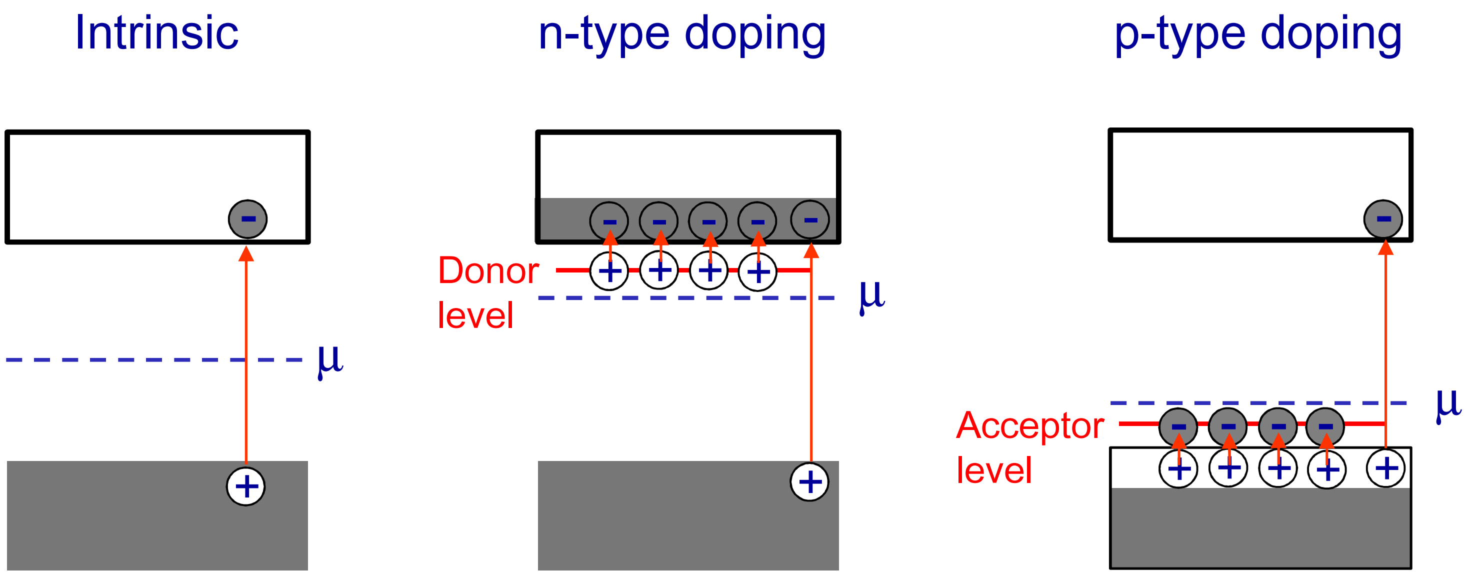


- Energy-band point of view



Only need to overcome a much smaller energy gap

Impurity level and chemical potential



The law of mass action

- At a given *T*, it suffices to know the density of one carrier to determine that of the other.

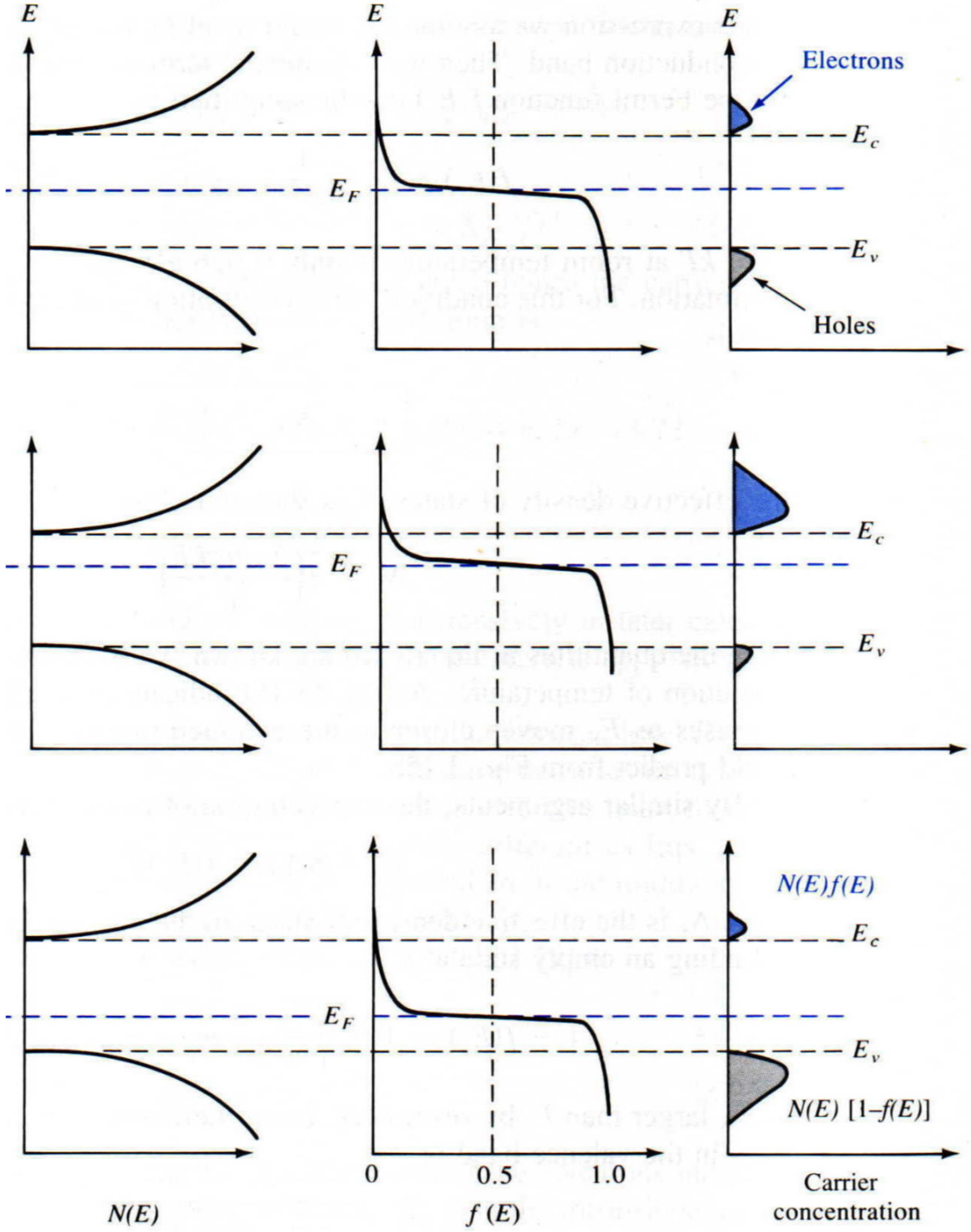
Upon doping,

$$np = n_i p_i (= n_i^2)$$

- Thus, one only needs to shift the chemical potential to account for the doping,

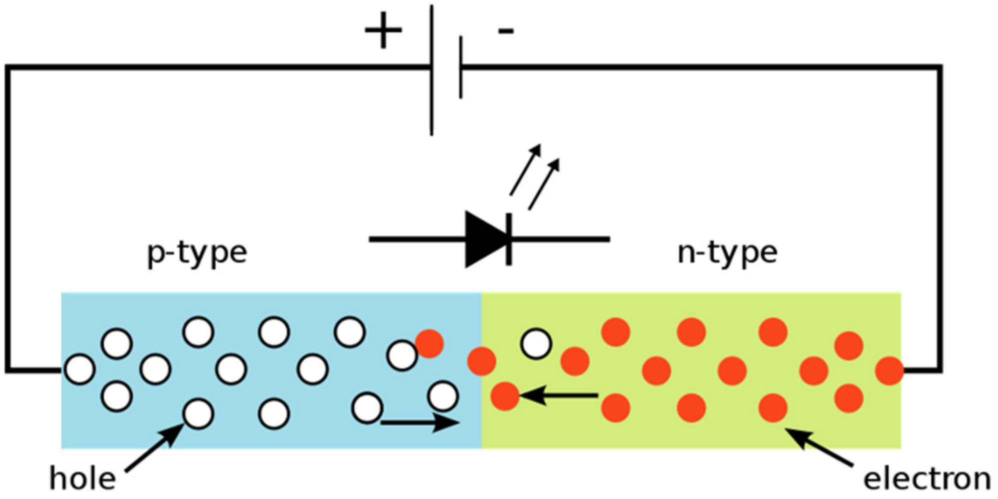
$$n = N_C e^{(\mu - E_G)/k_B T} = n_i e^{(\mu - \mu_i)/k_B T}$$

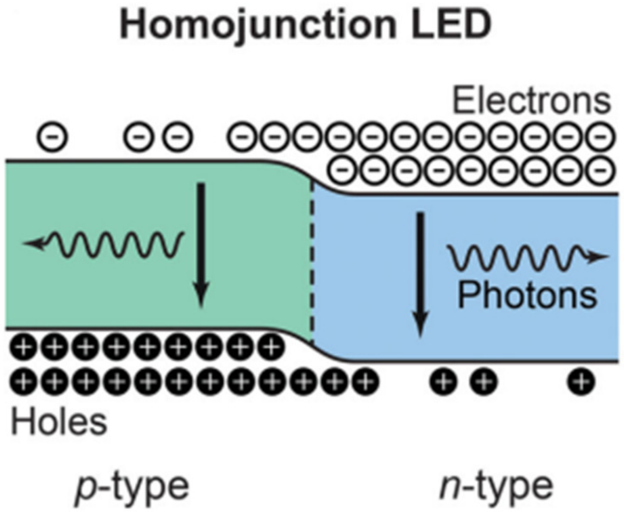
$$p = N_V e^{-\mu/k_B T} = n_i e^{(\mu_i - \mu)/k_B T}$$

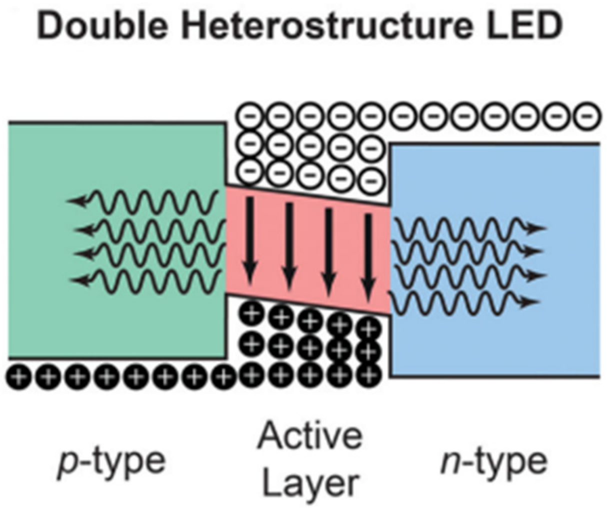


B.G. Streetman, Solid State Electronic Devices

Light emitting diode




Homojunction LED


Double Heterostructure LED

The invention of blue-light LED

GaN can emit blue light because of its large band gap (3.4 eV).

- 1994 Efficient blue-light LED, Shuji Nakamura
- 1997 Blue-light laser, Shuji Nakamura

中村修二

Before

After

See “Interview with Nakamura”: Scientific American, July, 2000

THE MILLENNIUM
TECHNOLOGY
PRIZE 2006

2014

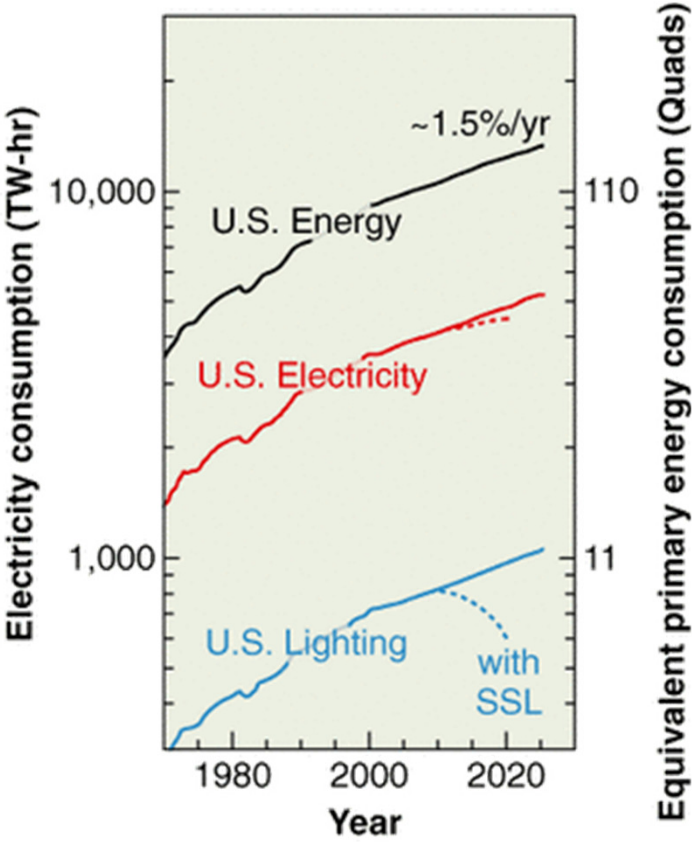
Solid-state lighting

Advantage

- Energy efficiency
- Non-toxic (no mercury)
- Robust, long-life
- Versatile: multi-color, instant start, can be pulsed, small size, low energy requirement, intelligent lighting system

Disadvantage

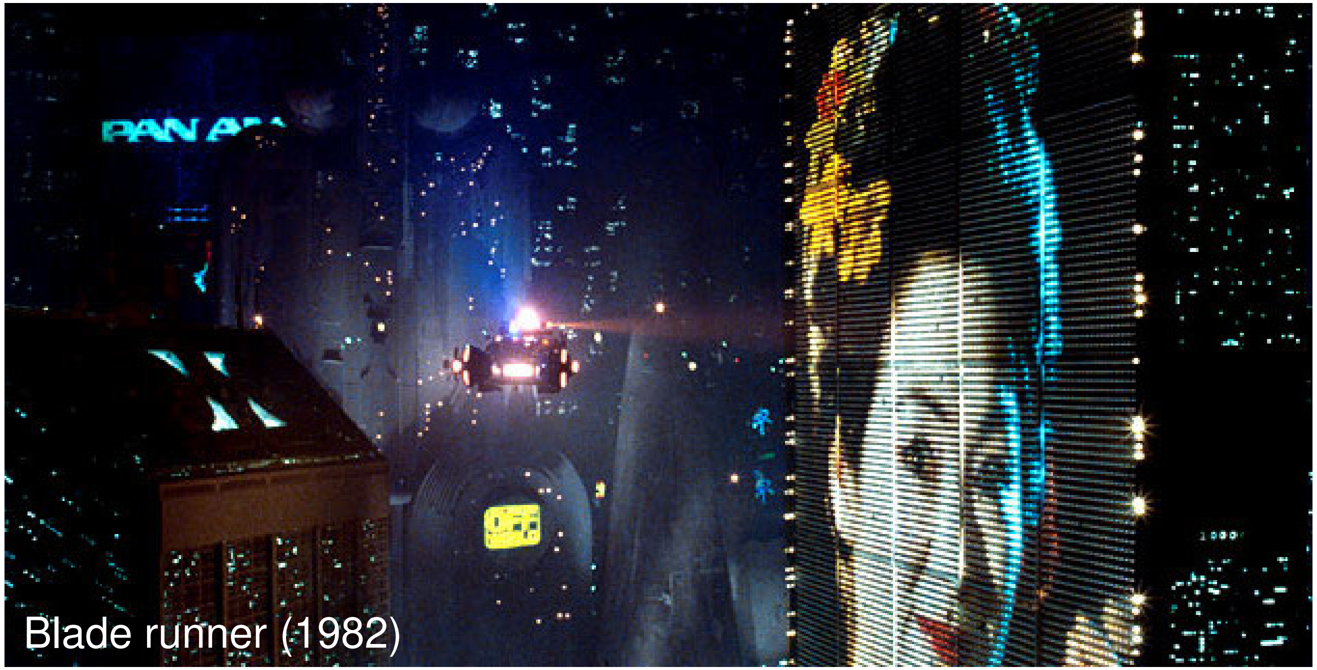
- Price
- LED mount needs good heat dissipation
- Light pollution



UV Water Purifier

Kerosene lighting and firewood are used by 1/3 of the world; they cause countless fires and are very inefficient.

LED-backlit LCD TV



Blade runner (1982)