

Technische Universität Graz

# 8. Semiconductors

#### **Boltzmann approximation**

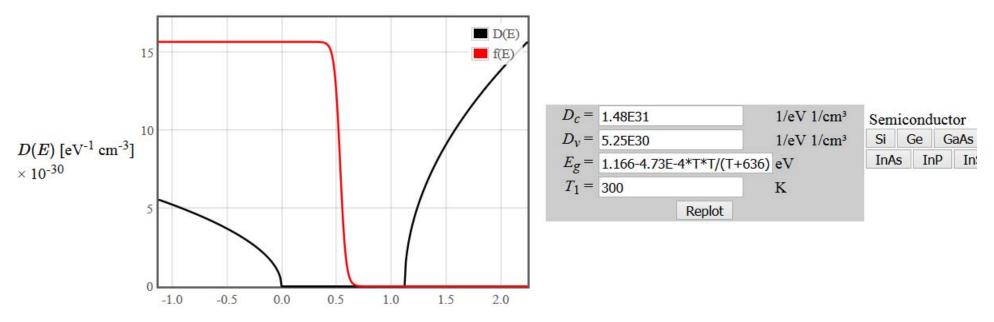
of the valence band and the bottom of the conduction band the density of states of a semiconductor can be approximated as,

$$D(E) = \left\{ egin{aligned} D_v \sqrt{E_v - E}, & ext{for } E < E_v \ 0, & ext{for } E_v < E < E_c \ D_c \sqrt{E - E_c}, & ext{for } E_c < E \end{aligned} 
ight.$$

and  $D_c$  are constants that describe the form of the density of states near the band edges. Often in the literature, these constants are given in terms of the sses'  $m_h^*$  and  $m_e^*$  or the 'effective density of states at 300 K'  $N_v(300)$  and  $N_c(300)$ . The relations to  $D_v$  and  $D_c$  are,

$$D_v = rac{(2m_h^*)^{3/2}}{2\pi^2\hbar^3} = rac{\sqrt{\pi}N_v(300)}{2(k_BT)^{3/2}}, \qquad D_c = rac{(2m_e^*)^{3/2}}{2\pi^2\hbar^3} = rac{\sqrt{\pi}N_c(300)}{2(k_BT)^{3/2}}.$$

w shows the density of states of various semiconductors in this approximation. The Fermi function is plotted as well. At low energies the value of the tes are occupied. At high energies the Fermi function goes to zero and those states are unoccupied. In the limit of low temperture, the chemical potent  $\tan \mu = E_g/2$ . As the temperature increases, the chemical potential moves towards the band with the lower density of states.



http://lampx.tugraz.at/~hadley/ss1/semiconductors/boltzmann.php

# The electrical contribution to the thermodynamic properties of insulators depend on band edges

#### Boltzmann approximation

The table below gives the contribution of electrons in intrinsic semiconductors and insulators to some thermodynamic quantities. These results where calculated in the Boltzmann approximation where it is assumed that the chemical potential lies in the band gap more than  $3k_BT$  from the band edge. The electronic contribution to the thermodynamic quantities are usually much smaller than the contribution of the phonons and thus the electronic components are often simply ignored.

	1-d	2-d		
Density of states $m_e^*$ and $m_h^*$ are 'density of states' effective masses	$\frac{1}{\hbar\pi} \sqrt{\frac{2m_h^*}{(E_v - E)}} \qquad E < E_v$ $D(E) = \qquad 0 \qquad E_v < E < E_c \qquad \mathbf{J}^{-1} \mathbf{m}^{-1}$ $\frac{1}{\hbar\pi} \sqrt{\frac{2m_e^*}{(E - E_c)}} \qquad E > E_c$	$\frac{m_h^*}{\hbar^2 \pi} H(E_v - E)  E < E_v$ $D(E) =  0  E_v < E < E_c  J^{-1} \text{ m}^{-2}$ $\frac{m_e^*}{\hbar^2 \pi} H(E - E_c)  E > E_c$ $H(x) = 0  \text{for}  x < 0 \text{ and } H(x) = 1  \text{for}  x > 0$		
Density of states $N_{ m v}$ and $N_{ m c}$ are the effective densities of states	$N_{\nu}(300)\sqrt{\frac{2}{300\pi k_{B}(E_{\nu}-E)}}  E < E_{\nu}$ $D(E) =  0  E_{\nu} < E < E_{c}  J^{-1} \text{ m}^{-1}$ $N_{c}(300)\sqrt{\frac{2}{300\pi k_{B}(E-E_{c})}}  E > E_{c}$	$D(E) = \frac{N_{\nu}(300)}{300k_{B}}H(E_{\nu} - E)  E < E_{\nu}$ $D(E) = 0  E_{\nu} < E < E_{c}  J^{-1} \text{ m}^{-2}$ $\frac{N_{c}(300)}{300k_{B}}H(E - E_{c})  E > E_{c}$		
Density of electrons in the conduction band $m = \int_{-\infty}^{\infty} D(E) f(E) dE$	$n = \sqrt{\frac{m_e^* k_B T}{\hbar^2 \pi}} \exp\left(\frac{\mu - E_c}{k_B T}\right)  \mathbf{m}^{-1}$	$n = \frac{m_e^* k_B T}{\hbar^2 \pi} \exp\left(\frac{\mu - E_c}{k_B T}\right)  \text{m}^{-2}$		
$n = \int_{E_{\epsilon}} D(E) f(E) dE$	$= N_c \exp \left( \frac{\mu - E_c}{k_B T} \right)$	$=N_c \exp\left(rac{\mu-E_c}{k_BT} ight)$		
Density of holes in the valence band $E$ ,	$p = \sqrt{\frac{m_h^* k_B T}{\hbar^2 \pi}} \exp\left(\frac{E_{\nu} - \mu}{k_B T}\right)  \mathbf{m}^{-1}$	$p = \frac{m_h^* k_B T}{\hbar^2 \pi} \exp\left(\frac{E_v - \mu}{k_B T}\right)  \mathbf{m}^{-2}$		
$p = \int_{-\infty}^{\infty} D(E) (1 - f(E)) dE$	$= N_{\nu} \exp \left( \frac{\mu - E_{c}}{k_{-}T} \right)$	$= N_{\nu} \exp \left( \frac{\mu - E_{c}}{k_{-}T} \right)$		

#### Intrinsic semiconductors

In the Boltzmann approximation, the density of states of a semiconductor is,

$$D(E) = \left\{ egin{array}{ll} rac{{{{\left( {2m_h^*} 
ight)}^{3/2}}}}{{2{\pi ^2}\hbar ^3}}\sqrt {E_v - E}, & ext{if } E < E_v \ 0, & ext{if } E_v < E < E_c \ rac{{{{\left( {2m_e^*} 
ight)}^{3/2}}}}{{2{\pi ^2}\hbar ^3}}\sqrt {E - E_c}, & ext{if } E_c < E \end{array} 
ight.$$

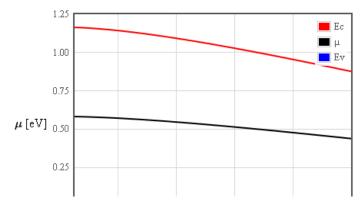
Here  $m_e^*$  and  $m_h^*$  are the 'density of states effective masses' for electrons and holes. Usually in the literature, effective density of states at 300 K is given instead of the 'density of states effective masses'. The relationship between the two is,

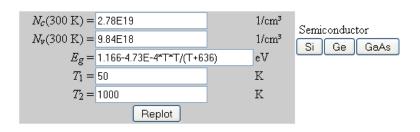
$$m_{h}^{*} = rac{\pi \hbar^{2}}{300 k_{B}} \left(\sqrt{2} N_{v}(300)
ight)^{2/3} \ m_{e}^{*} = rac{\pi \hbar^{2}}{300 k_{B}} \left(\sqrt{2} N_{c}(300)
ight)^{2/3}$$

In an intrinsic semiconductor, the density of electrons equals the density of holes,  $n=p=n_i=\sqrt{N_c \left(\frac{T}{300}\right)^{3/2}N_v \left(\frac{T}{300}\right)^{3/2}}\exp\left(\frac{-E_g}{2k_BT}\right)$ .

By setting the concentration of electrons equal to the concentration of holes, it is possible to solve for the chemical potential. The bandgap of most semiconductors is temperature dependent. The form below lets you input the temperature dependance of the bandgap. The bandgaps for some semiconductors can be loaded into the form with the buttons on the right.

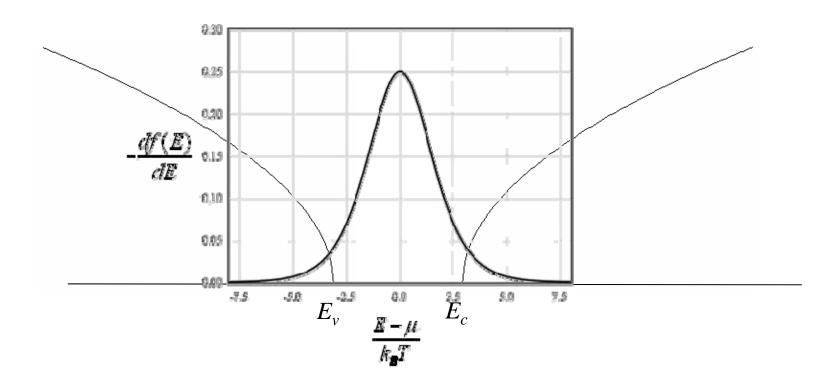
$$n = N_c(300) \left(rac{T}{300}
ight)^{3/2} \exp\left(rac{\mu - E_c}{k_B T}
ight) = p = N_v(300) \left(rac{T}{300}
ight)^{3/2} \exp\left(rac{E_v - \mu}{k_B T}
ight)$$
 ,  $\mu = rac{E_v + E_c}{2} + k_B T \ln\left(rac{N_v(300)}{N_c(300)}
ight)$  .





http://lamp.tu-graz.ac.at/~hadley/ss1/semiconductors/intrinsic.php

### Narrow bandgap semiconductors



Use the programs for metals for small bandgap semiconductors.

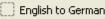














- Silicon - Germanium Si Ge

- Gallium Phosphide - Gallium Arsenide GaP GaAs:

- Indium Arsenide InAs C - Diamond

- Indium Antimonide GaSb - Gallium Antimonide InSb

InP - Indium Phosphide - Gallium Arsenide Antimonide GaAs<sub>1-x</sub>Sb<sub>x</sub>

Al<sub>x</sub>Ga<sub>1-x</sub>As - Aluminium Gallium Arsenide

- Aluminium Nitride - Indium Nitride AlN. InN - Gallium Nitride - Boron Nitride BN GaN

#### We are going to add new data for:

 $Ga_xIn_{1-x}As_ySb_{1-y}$ - Gallium Indium Arsenide Antimonide  $Ga_xIn_{1-x}P$ - Gallium Indium Phosphide

 $Ga_xIn_{1-x}As$ - Gallium Indium Arsenide Ga<sub>x</sub>In<sub>1-x</sub>Sb - Gallium Indium Antimonide - Indium Arsenide Antimonide  $InAs_{1-x}Sb_x$  $Ga_xIn_{1-x}As_vP_{1-v}$ - Gallium Indium Arsenide Phosphide

- Silicon Germanium SiC - Silicon Carbide Si<sub>1-x</sub>Ge<sub>x</sub>

### Effective Masses

#### Electrons:

The surfaces of equal energy are ellipsoids.

 $m_1 = 0.98 m_0$ 

 $m_t = 0.19 m_0$ 

Effective mass of density of states  $m_c = 0.36m_o$ 

There are 6 equivalent valleys in the conduction band.

 $m_{cc}=0.26m_{o}$ 

#### Holes:

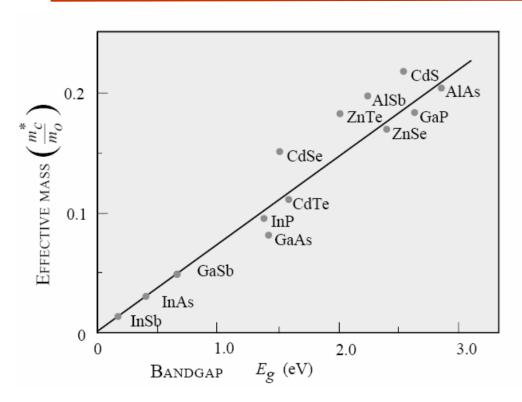
Heavy  $m_h = 0.49 m_0$ 

Light  $m_{lp} = 0.16 m_o$ 

Split-off band  $m_{so} = 0.24 m_o$ 

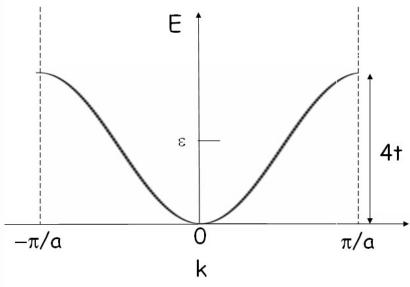
Effective mass of density of states  $m_{V} = 0.81 m_{O}$ 

### Large gap -> large effective mass



$$m^* = \frac{\hbar^2}{\frac{d^2 E}{dk^2}}$$

narrow bands -> large effective mass



$$E_k = \varepsilon - 2t \cos(ka)$$

$$\frac{d^2E}{dk^2} = 2ta^2$$
\* 1

$$m^* \sim \frac{1}{t}$$

# Measuring the effective mass

Cyclotron resonance 
$$\omega_c = \frac{eB}{m^*}$$

Resonant absorption occurs when rf waves with the cyclotron resonance frequency are applied. This can be used to experimentally determine the effective mass.

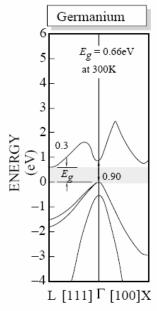
Knowing the effective mass, the scattering time can be calculated from the measured conductivity.

$$\sigma = \frac{ne^2\tau_{sc}}{m^*}$$

### Direct and indirect band gaps

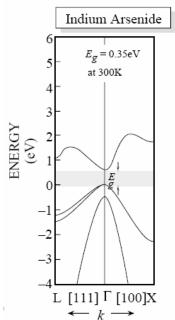
indirect bandgap  $\Delta k \neq 0$ 

phonons are emitted



direct bandgap:  $\Delta k = 0$ 

photons can be emitted

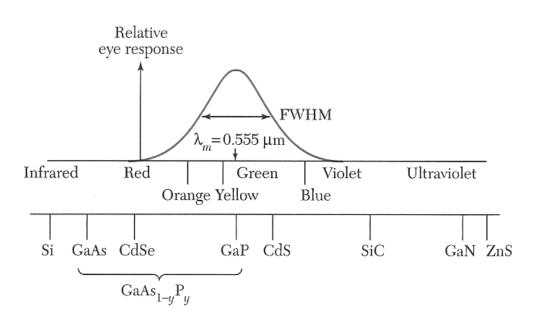


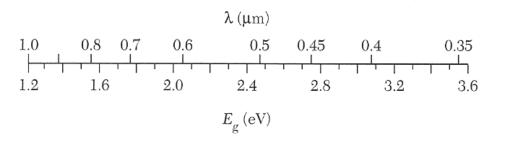
Momentum must be conserved when photons are absorbed or emitted.

TABLE 1 Common III-V materials used to produce LEDs and their emission wavelengths.

Material	Wavelength (nm)		
InAsSbP/InAs	4200		
InAs	3800		
GaInAsP/GaSb	2000		
GaSb	1800		
$Ga_x In_{1-x} As_{1-y} P_y$	1100-1600		
$Ga_{0.47}In_{0.53}As$	1550		
$Ga_{0.27}In_{0.73}As_{0.63}P_{0.37}$	1300		
GaAs:Er,InP:Er	1540		
Si:C	1300		
GaAs:Yb,InP:Yb	1000		
$Al_xGa_{1-x}As:Si$	650-940		
GaAs:Si	940		
$Al_{0.11}Ga_{0.89}As:Si$	830		
Al <sub>0.4</sub> Ga <sub>0.6</sub> As:Si	650		
$GaAs_{0.6}P_{0.4}$	660		
$GaAs_{0.4}P_{0.6}$	620		
$GaAs_{0.15}P_{0.85}$	590		
$(Al_xGa_{1-x})_{0.5}In_{0.5}P$	655		
GaP	690		
GaP:N	550-570		
$Ga_xIn_{1-x}N$	340,430,590		
SiC	400-460		
BN	260,310,490		

### Light emitting diodes





### Extrinsic semiconductors

The introduction of impurity atoms that can and electrons or holes is called doping.

n-type: donor atoms contribute electrons to the conduction band.

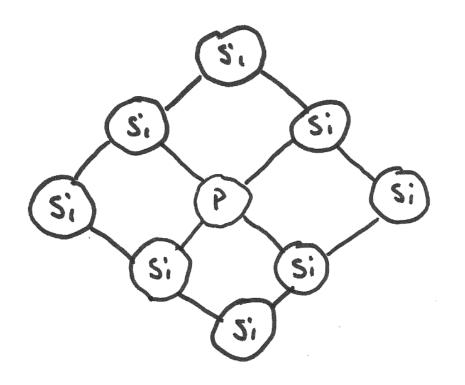
Examples: P, As in Si.

p-type: acceptor atoms contribute holes to the valence band.

Examples: B, Ga, Al in Si.

	ША	IVA	VA	VIA
	В	C	N	O°
IIB	Al	Si <sup>14</sup>	P 15	S 16
Zn	Ga	Ge	As	Se
Cd	In	Sn Sn	Sb	Te

### Ionization of dopants



Easier to ionize a P atom in Si than a free P atom

$$E_n = -\frac{me^4}{8\varepsilon_0^2 h^2 n^2}$$

Ionization energy is smaller by a factor:  $\frac{m^*}{m} \left( \frac{\varepsilon_0}{\varepsilon_r \varepsilon_0} \right)^2$ 

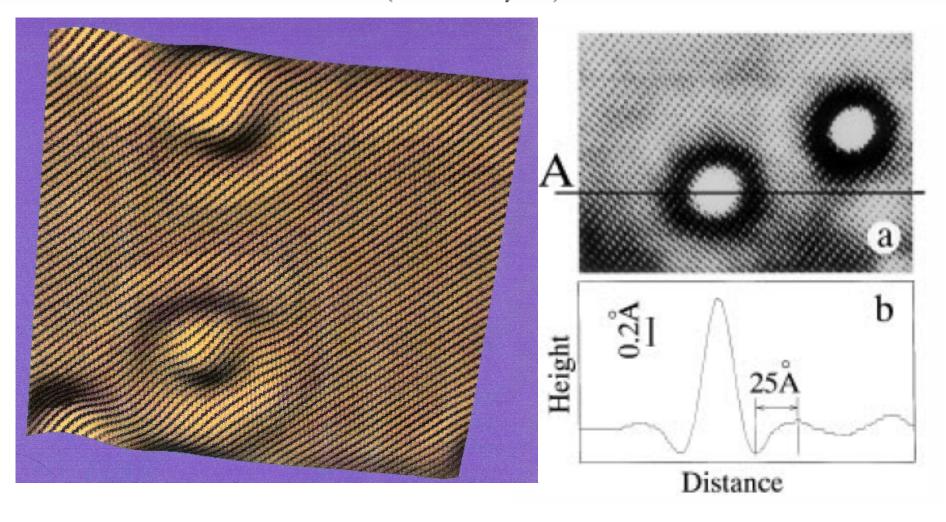
Ionization energy  $\sim 25 \text{ meV}$ 

# Direct Observation of Friedel Oscillations around Incorporated Si<sub>Ga</sub> Dopants in GaAs by Low-Temperature Scanning Tunneling Microscopy

M. C. M. M. van der Wielen, A. J. A. van Roij, and H. van Kempen

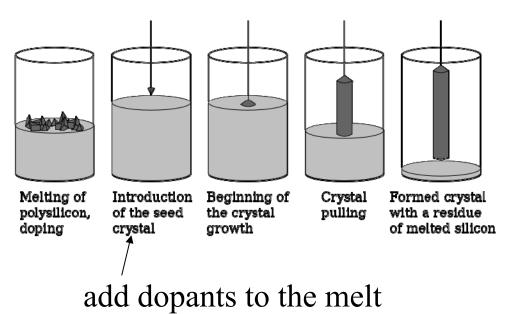
Research Institute for Materials, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

(Received 25 July 1995)



# Crystal growth

#### **Czochralski Process**





images from wikipedia

# Crystal growth

#### **Float zone Process**

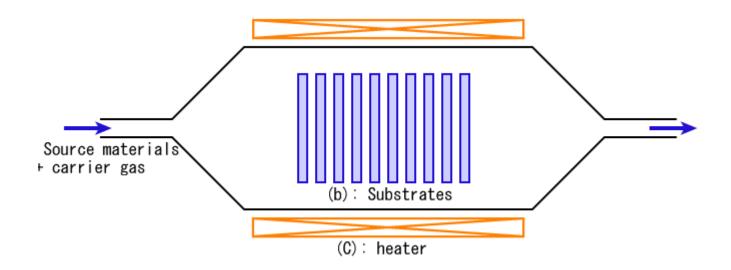
Neutron transmutation

$$^{30}$$
Si + n  $\rightarrow$   $^{31}$ Si +  $\gamma$   
 $^{31}$ Si  $\rightarrow$   $^{31}$ P +  $\beta$ 



image from wikipedia

### Chemical vapor deposition



Epitaxial silicon CVD SiH<sub>4</sub> (silane) or SiH<sub>2</sub>Cl<sub>2</sub> (dichlorosilane) PH<sub>3</sub> (phosphine) for n-doping or B<sub>2</sub>H<sub>6</sub> (diborane) for p-doping.

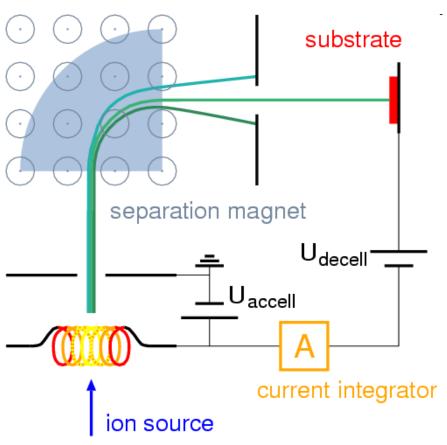
# Gas phase diffusion



AsH<sub>3</sub> (Arsine) or PH<sub>3</sub> (phosphine) for n-doping B<sub>2</sub>H<sub>6</sub> (diborane) for p-doping.

# Ion implantation



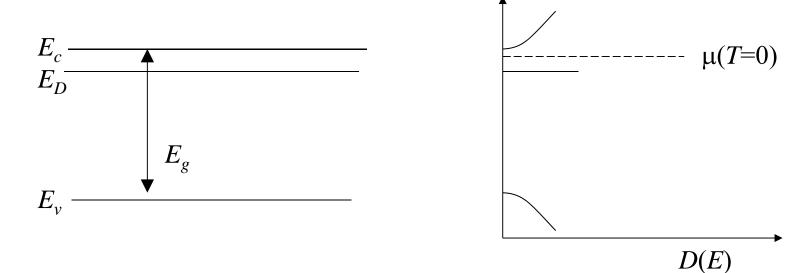


Implant at 7° to avoid channeling

### Donors

Five valence electrons: P, As

States are added in the band gap just below the conduction band



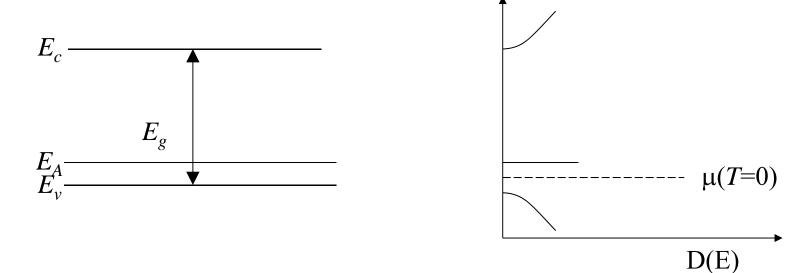
n-type:  $n \sim N_D$  Many more electrons in the conduction band than holes in the valence band.

majority carriers: electrons; minority carriers: holes

### Acceptors

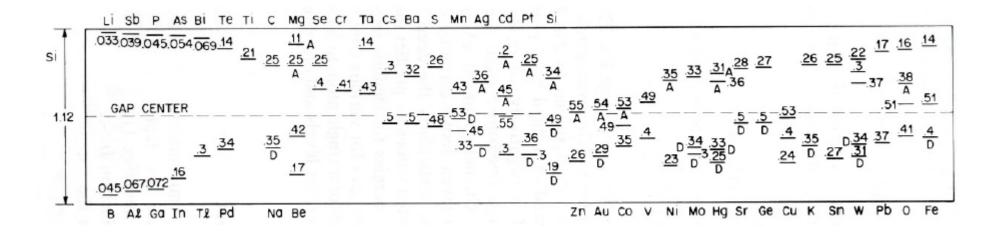
Three valence electrons: B, Al, Ga

States are added in the band gap just above the valence band



p-type:  $p \sim N_A$  Many more holes in the valence band than electrons in the conduction band.

majority carriers: holes; minority carriers: electrons



Source: Semiconductor Devices Physics and Technology, S.M. Sze, 1985

# Donor and Acceptor Energies

Semiconductor	Donor	Energy (meV)
	Li	33
Si	Sb	39
51	P	45
	As	54
	Li	9.3
Ge	Sb	9.6
J Ge	P	12
	As	13
	Si	5.8
GaAs	Ge	6.0
GaAs	S	6.0
	Sn	6.0

Semiconductor	Acceptor	Energy (meV)
	В	45
Si	A1	67
21	Ga	72
	In	160
	В	10
Ge	A1	10
J Ge	Ga	11
	In	11
	C	26
GaAs	Be	28
GaAs	Mg	28
	Si	35

Energy below the conduction band

Energy above the valence band

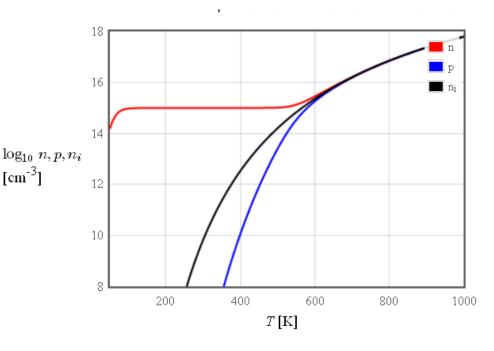
### n-type

n-type  $N_D > N_A$ ,  $p \sim 0$ 

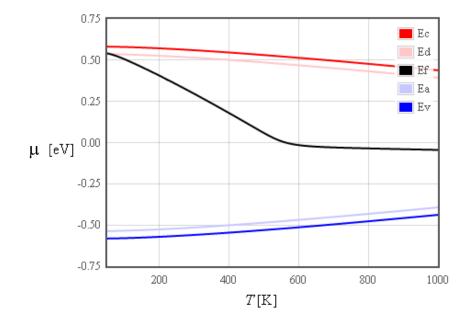
$$n = N_D = N_c \exp\left(\frac{\mu - E_c}{k_B T}\right)$$

$$\mu = E_c - k_B T \ln \left( \frac{N_c}{N_D} \right)$$

For n-type,  $n \sim$  density of donors,  $p = n_i^2/n$ 



 $[cm^{-3}]$ 



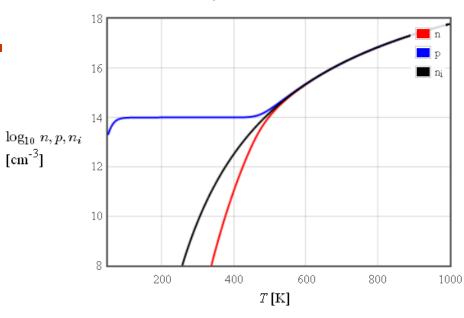
### p-type

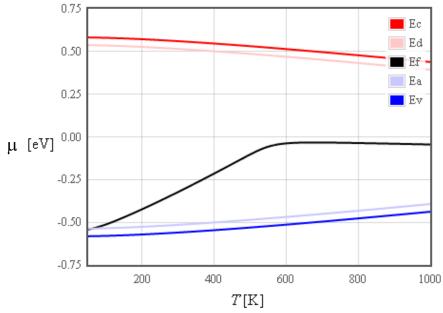
p-type 
$$N_A > N_D$$
,  $n \sim 0$ 

$$p = N_A = N_v \exp\left(\frac{E_v - \mu}{k_B T}\right)$$

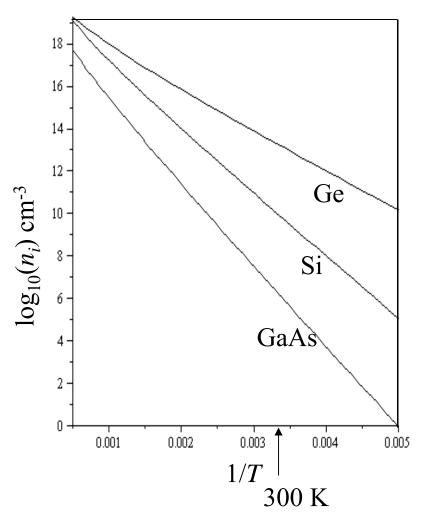
$$\mu = E_v + k_B T \ln \left( \frac{N_v}{N_A} \right)$$

For p-type,  $p \sim$  density of acceptors,  $n = n_i^2/p$ 



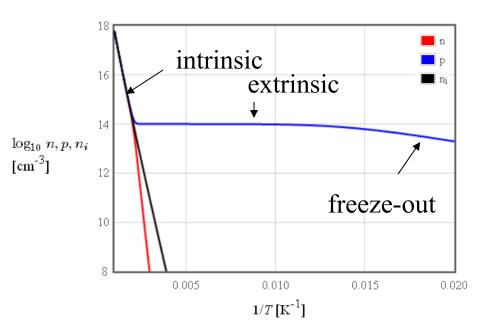


### Intrinsic semiconductors



$$n_i = \sqrt{N_v N_c} \exp\left(-\frac{E_g}{2k_B T}\right)$$

### Extrinsic semiconductors



At high temperatures, extrinsic semiconductors have the same temperature dependence as intrincic semiconductors.

## Ionized donors and acceptors

For 
$$E_v + 3k_BT < \mu < E_c$$
-  $3k_BT$  Boltzmann approximation

$$N_D^+ = \frac{N_D}{1 + 2 \exp\left(\frac{\mu - E_D}{k_B T}\right)}$$

$$N_A^- = \frac{N_A}{1 + 4 \exp\left(\frac{E_A - \mu}{k_B T}\right)}$$

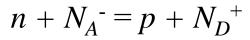
4 for materials with light holes and heavy holes (Si) 2 otherwise

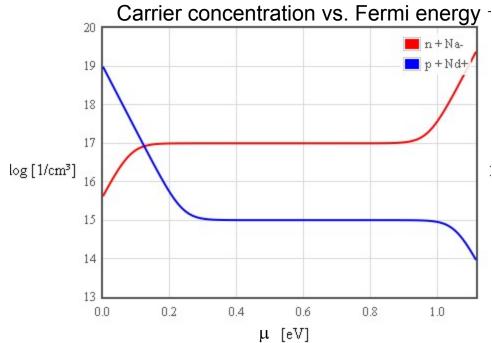
$$N_D = \text{donor density cm}^{-3}$$
  $N_D^+ = \text{ionized donor density cm}^{-3}$ 

$$N_A = \text{donor density cm}^{-3}$$
  $N_A^- = \text{ionized donor density cm}^{-3}$ 

Mostly, 
$$N_D^+ = N_D$$
 and  $N_A^- = N_A$ 

# Charge neutrality



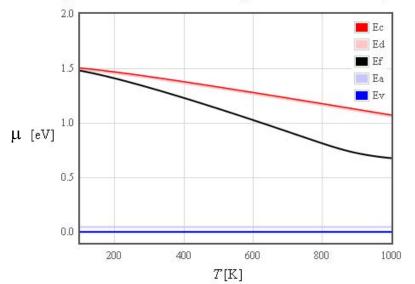


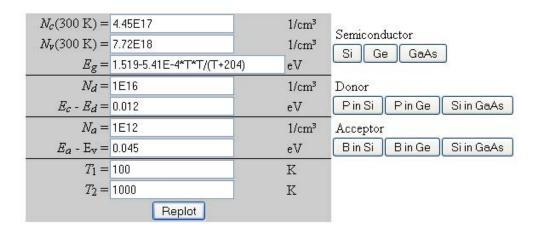
```
for ($i=0; $i<500; $i++) {
    $Ef = $i*$Eg/500;
    $n=$Nc*pow($T/300,1.5) *exp(1.6022E-19*($Ef-$Eg)/(1.38E-23*$T));
    $p=$Nv*pow($T/300,1.5) *exp(1.6022E-19*(-$Ef)/(1.38E-23*$T));
    $Namin = $Na/(1+4*exp(1.6022E-19*($Ea-$Ef)/(1.38E-23*$T)));
    $Ndplus = $Nd/(1+2*exp(1.6022E-19*($Ef-$Ed)/(1.38E-23*$T)));
}</pre>
```

$E_f$	n	p	$N_d^+$	$N_a^{-}$	$\log(n+N_a^-)$	log(p+N <sub>d</sub> +)
0	4.16629283405	9.84E+18	1E+15	4.19743393218E+15	15.622983869	18.9930392318
0.00224	4.54358211887	9.0229075682E+18	1E+15	4.56020949614E+15	15.6589847946	18.9553946382
0.00448	4.95503779816	8.27366473417E+18	1E+15	4.95271809535E+15	15.694843609	18.9177504064
0.00672	5.40375389699	7.58663741327E+18	1E+15	5.37710747619E+15	15.7305487171	18.8801065693
ሳ ሳሳዕላሪ	5 00210450701	C 05CC502C215T+10	17:15	E 0256000025T   15	15 7660076057	10 0494691696

#### Fermi energy vs. temperature

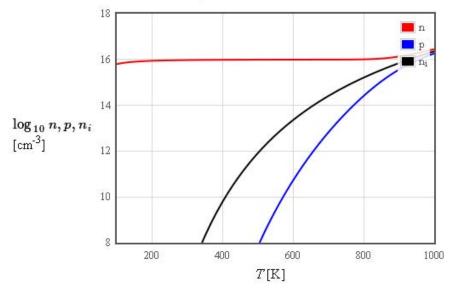
Fermi energy of an extrinsic semiconductor is plotted as a function of temperature. At each temperature the Fermi energy was calculated by requiring that charge neutrality be satisfied.

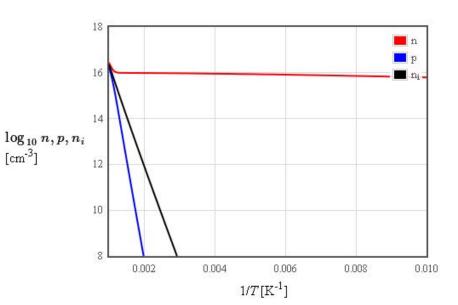




Once the Fermi energy is known, the carrier densities n and p can be calculated from the formulas,  $n = N_c \left(\frac{T}{300}\right)^{3/2} \exp\left(\frac{E_F - E_c}{k_B T}\right)$  and  $p = N_v \left(\frac{T}{300}\right)^{3/2} \exp\left(\frac{E_v - E_F}{k_B T}\right)$ .

The intrinsic carrier density is  $n_i = \sqrt{N_c \left(rac{T}{300}
ight)^{3/2} N_v \left(rac{T}{300}
ight)^{3/2}} \exp\left(rac{-E_g}{2k_BT}
ight)$ .





# pn junction

#### under normal operation conditions

p-type

$$N_A > N_D$$
  $p = N_A - N_D$ 
 $E_c$ 
 $E_v$ 

$$n = \frac{n_i^2}{p} = \frac{n_i^2}{N_A - N_D}$$

$$\mu = E_v + k_B T \ln \left( \frac{N_v}{N_A - N_D} \right)$$

n-type

$$N_D > N_A$$
  $n = N_D - N_A$ 

$$E_c$$

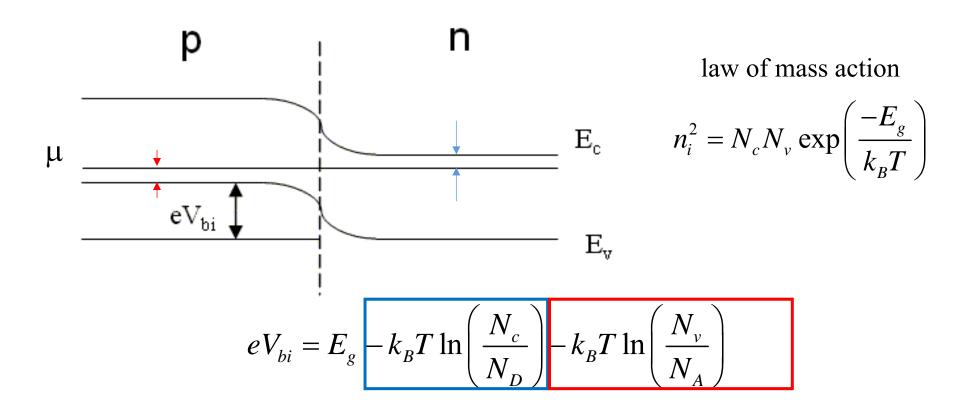
$$E_v$$

$$p = \frac{n_i^2}{n} = \frac{n_i^2}{N_D - N_A}$$

$$\mu = E_v + k_B T \ln \left( \frac{N_v}{N_A - N_D} \right) \qquad \mu = E_c - k_B T \ln \left( \frac{N_c}{N_D - N_A} \right)$$

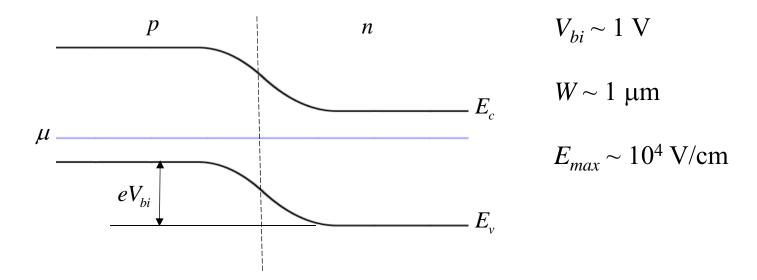
Semiconductor devices Kittel p. 503 - 512

# V<sub>bi</sub> built-in voltage



$$eV_{bi} = E_g - k_B T \ln \left( \frac{N_c N_v}{N_D N_A} \right) = k_B T \ln \left( \frac{N_D N_A}{n_i^2} \right)$$

# p and n profiles



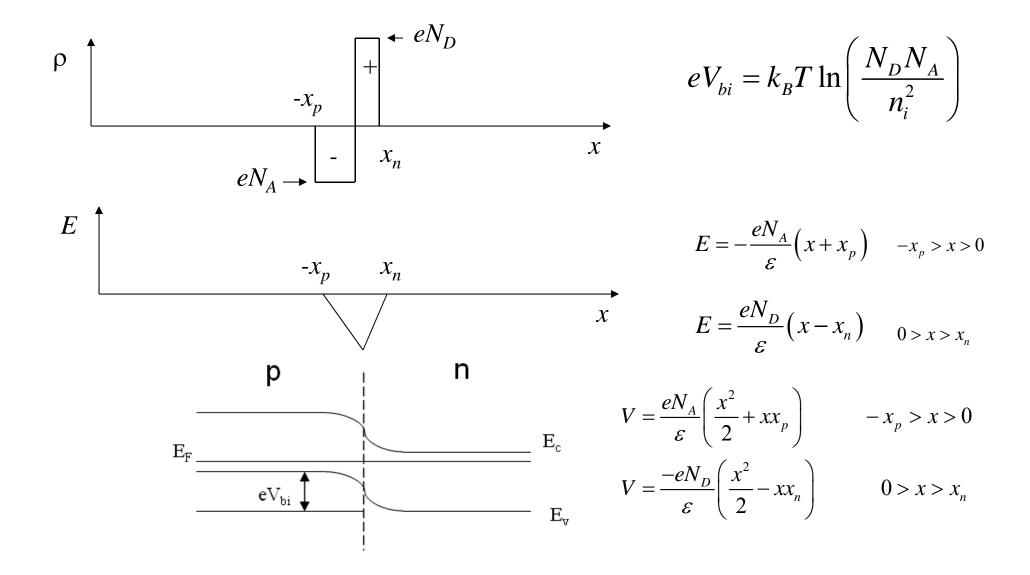
$$p = N_v \exp\left(\frac{E_v - \mu}{k_B T}\right)$$

$$n = N_c \exp\left(\frac{\mu - E_c}{k_B T}\right)$$

The electric field pushes the electrons towards the n-region and the holes towards the p-region.

Diffusion sends electrons towards the p-region and holes towards the n-region.

# depletion approximation

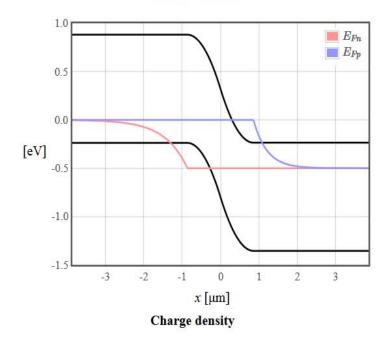


#### Abrupt pn junctions in the depletion approximation

In an abrupt pn junction, the doping changes abruptly from p to n. It is common to solve for the band bending, the local electric field, the carrier concentration profiles, and the local conductivity in the depletion approximation. In this approximation it is assumed that there is a depletion width W around the transition from p to n where the charge carrier densities are negligible. Outside the depletion width the charge carrier densities are equal to the doping densities so that the semiconductor is electrically neutral outside the depletion width. Using this approximation it is possible to calculate the important properties of the pn junction.

$$E_g=$$
 1.12 eV  $W=$  1.72 μm  $x_p=$  -0.861 μm  $x_n=$  0.861 μm  $V_{bi}=$  0.618 V  $C_j=$  6.17 nF/cm² 
$$D_p=$$
 12.4 cm²/s  $D_n=$  34.9 cm²/s  $L_p=$  0.352 μm  $L_n=$  0.591 μm

#### **Band diagram**



#### **Current-Voltage Characteristics**

