

# Semiconductors

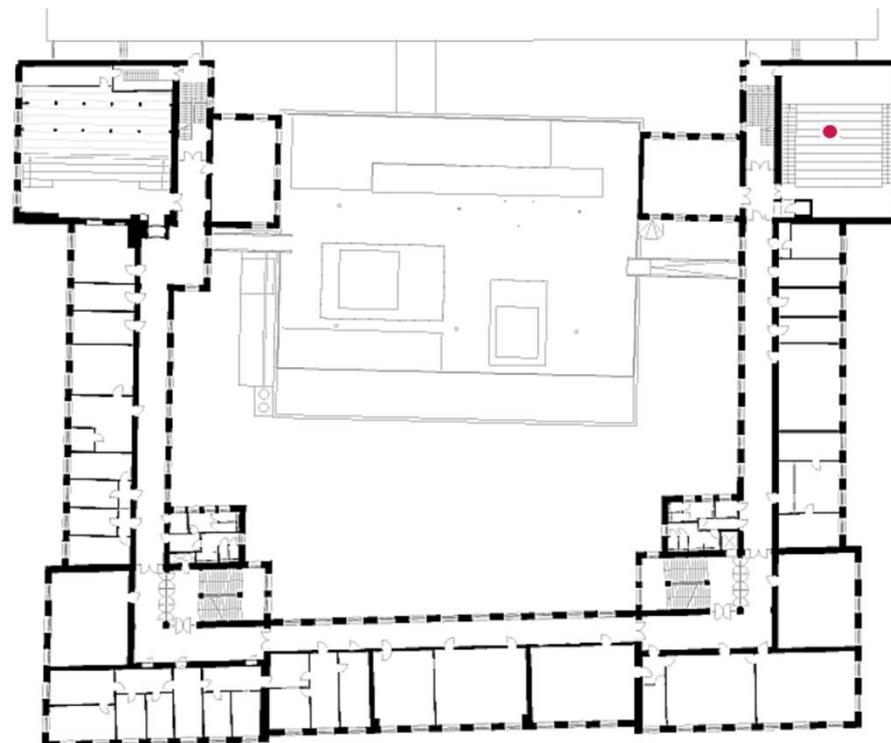
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# Exam

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HS B 10:15 – 11:15

1 A4 handwritten notes



# Boltzmann Approximation

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## Boltzmann approximation

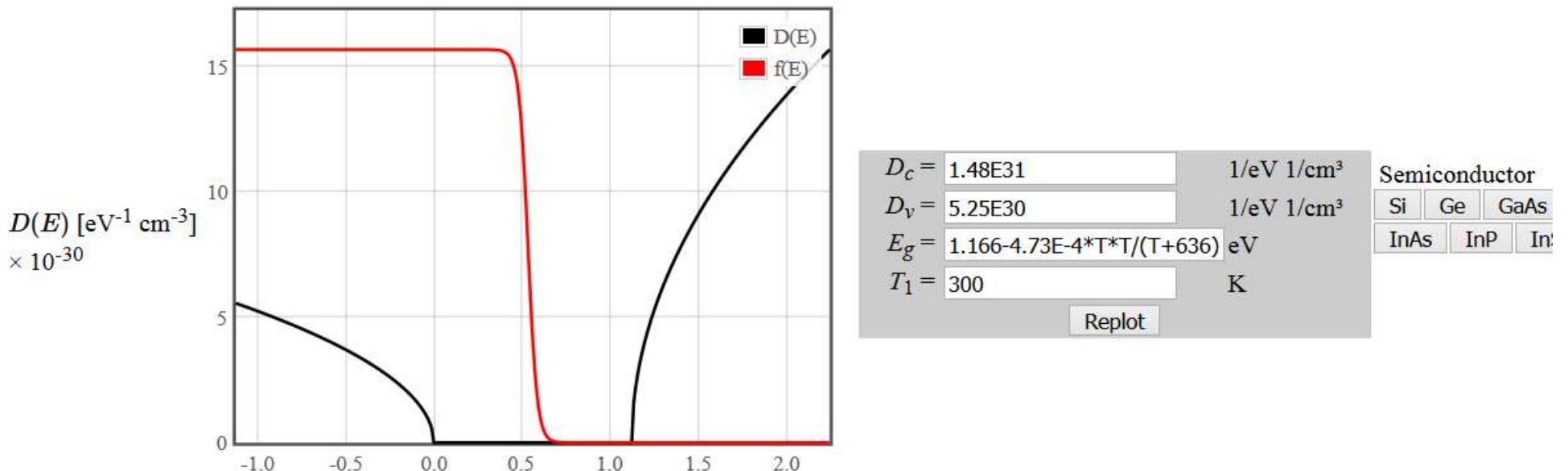
of the valence band and the bottom of the conduction band the density of states of a semiconductor can be approximated as,

$$D(E) = \begin{cases} D_v \sqrt{E_v - E}, & \text{for } E < E_v \\ 0, & \text{for } E_v < E < E_c \\ D_c \sqrt{E - E_c}, & \text{for } E_c < E \end{cases}$$

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 'masses'  $m_h^*$  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,

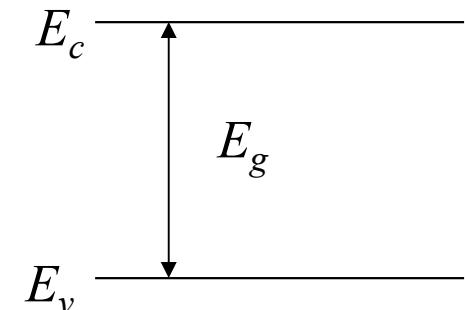
$$D_v = \frac{(2m_h^*)^{3/2}}{2\pi^2 \hbar^3} = \frac{\sqrt{\pi} N_v(300)}{2(k_B T)^{3/2}}, \quad D_c = \frac{(2m_e^*)^{3/2}}{2\pi^2 \hbar^3} = \frac{\sqrt{\pi} N_c(300)}{2(k_B T)^{3/2}}.$$

Now 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 states are occupied. At high energies the Fermi function goes to zero and those states are unoccupied. In the limit of low temperature, the chemical potential gap,  $\mu = E_g/2$ . As the temperature increases, the chemical potential moves towards the band with the lower density of states.



# Law of mass action

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$$np = N_c \exp\left(\frac{\mu - E_c}{k_B T}\right) N_v \exp\left(\frac{E_v - \mu}{k_B T}\right)$$
$$np = N_c N_v \exp\left(\frac{-E_g}{k_B T}\right)$$


For intrinsic semiconductors (no impurities)

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

intrinsic carrier density

# Chemical potential of an intrinsic semiconductor

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

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

$$\frac{2\mu}{k_B T} = \frac{E_c + E_v}{k_B T} + \ln\left(\frac{N_v}{N_c}\right)$$

$E_c$  —————  
 $\mu$  -----

$$\boxed{\mu = \frac{E_c + E_v}{2} + \frac{k_B T}{2} \ln\left(\frac{N_v}{N_c}\right)}$$

$E_v$  —————

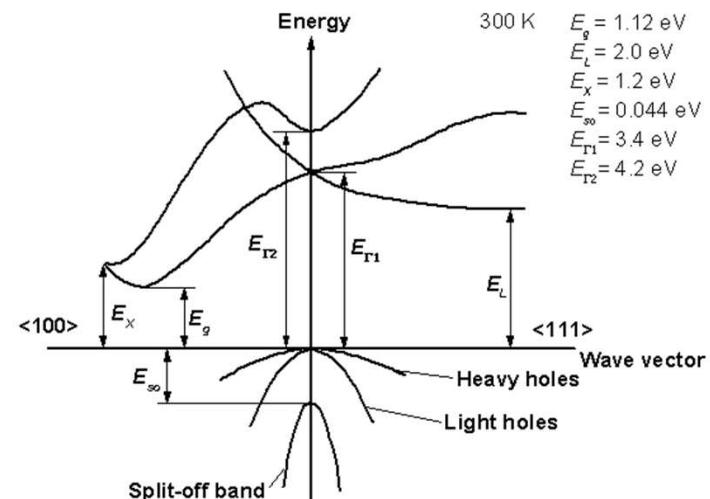
# New Semiconductor Materials. Biology systems.

## Characteristics and Properties

Semiconductors database	n,k InGaAsP	Levels	Equivalents	Bibliografic database
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## NSM Archive - Physical Properties of Semiconductors

Si	- Silicon	Ge	- Germanium
GaP	- Gallium Phosphide	GaAs	- Gallium Arsenide
InAs	- Indium Arsenide	C	- Diamond
GaSb	- Gallium Antimonide	InSb	- Indium Antimonide
InP	- Indium Phosphide	GaAs <sub>1-x</sub> Sb <sub>x</sub>	- Gallium Arsenide Antimonide
Al <sub>x</sub> Ga <sub>1-x</sub> As	- Aluminium Gallium Arsenide		
AlN	- Aluminium Nitride		
BN	- Boron Nitride		



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

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## Boltzmann approximation

The table below gives the contribution of electrons in intrinsic semiconductors and insulators to some thermodynamic quantities. These results were calculated in the Boltzmann approximation where it is assumed that the chemical potential lies in the band gap more than  $3k_B T$  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
<b>Density of states</b> $m_e^*$ and $m_h^*$ are 'density of states' effective masses	$D(E) = \begin{cases} \frac{1}{\hbar\pi} \sqrt{\frac{2m_h^*}{(E_\nu - E)}} & E < E_\nu \\ 0 & E_\nu < E < E_c \\ \frac{1}{\hbar\pi} \sqrt{\frac{2m_e^*}{(E - E_c)}} & E > E_c \end{cases} \text{ J}^{-1} \text{ m}^{-1}$	$D(E) = \begin{cases} \frac{m_h^*}{\hbar^2\pi} H(E_\nu - E) & E < E_\nu \\ 0 & E_\nu < E < E_c \\ \frac{m_e^*}{\hbar^2\pi} H(E - E_c) & E > E_c \end{cases} \text{ J}^{-1} \text{ m}^{-2}$ $H(x) = 0 \text{ for } x < 0 \text{ and } H(x) = 1 \text{ for } x > 0$
<b>Density of states</b> $N_\nu$ and $N_c$ are the effective densities of states	$D(E) = \begin{cases} N_\nu(300) \sqrt{\frac{2}{300\pi k_B(E_\nu - E)}} & E < E_\nu \\ 0 & E_\nu < E < E_c \\ N_c(300) \sqrt{\frac{2}{300\pi k_B(E - E_c)}} & E > E_c \end{cases} \text{ J}^{-1} \text{ m}^{-1}$	$D(E) = \begin{cases} \frac{N_\nu(300)}{300k_B} H(E_\nu - E) & E < E_\nu \\ 0 & E_\nu < E < E_c \\ \frac{N_c(300)}{300k_B} H(E - E_c) & E > E_c \end{cases} \text{ J}^{-1} \text{ m}^{-2}$
<b>Density of electrons in the conduction band</b> $n = \int_{E_c}^{\infty} D(E)f(E)dE$	$n = \sqrt{\frac{m_e^* k_B T}{\hbar^2 \pi}} \exp\left(\frac{\mu - E_c}{k_B T}\right) \text{ m}^{-1}$ $= N_c \exp\left(\frac{\mu - E_c}{k_B T}\right)$	$n = \frac{m_e^* k_B T}{\hbar^2 \pi} \exp\left(\frac{\mu - E_c}{k_B T}\right) \text{ m}^{-2}$ $= N_c \exp\left(\frac{\mu - E_c}{k_B T}\right)$
<b>Density of holes in the valence band</b> $p = \int_{-\infty}^{E_c} D(E)(1-f(E))dE$	$p = \sqrt{\frac{m_h^* k_B T}{\hbar^2 \pi}} \exp\left(\frac{E_\nu - \mu}{k_B T}\right) \text{ m}^{-1}$ $= N_\nu \exp\left(\frac{\mu - E_c}{k_B T}\right)$	$p = \frac{m_h^* k_B T}{\hbar^2 \pi} \exp\left(\frac{E_\nu - \mu}{k_B T}\right) \text{ m}^{-2}$ $= N_\nu \exp\left(\frac{\mu - E_c}{k_B T}\right)$

## Intrinsic semiconductors

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

$$D(E) = \begin{cases} \frac{(2m_h^*)^{3/2}}{2\pi^2\hbar^3} \sqrt{E_v - E}, & \text{if } E < E_v \\ 0, & \text{if } E_v < E < E_c \\ \frac{(2m_e^*)^{3/2}}{2\pi^2\hbar^3} \sqrt{E - E_c}, & \text{if } E_c < E \end{cases}$$

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,

$$m_h^* = \frac{\pi\hbar^2}{300k_B} \left( \sqrt{2}N_v(300) \right)^{2/3}$$

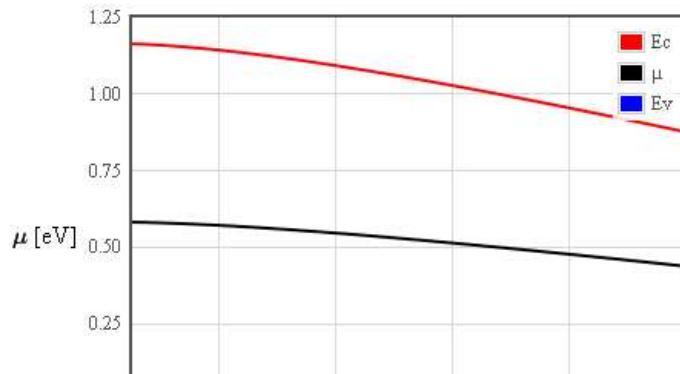
$$m_e^* = \frac{\pi\hbar^2}{300k_B} \left( \sqrt{2}N_c(300) \right)^{2/3}$$

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

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 dependence of the bandgap. The bandgaps for some semiconductors can be loaded into the form with the buttons on the right.

$$n = N_c(300) \left( \frac{T}{300} \right)^{3/2} \exp\left(\frac{\mu - E_c}{k_B T}\right) = p = N_v(300) \left( \frac{T}{300} \right)^{3/2} \exp\left(\frac{E_v - \mu}{k_B T}\right)$$

$$\mu = \frac{E_v + E_c}{2} + k_B T \ln\left(\frac{N_v(300)}{N_c(300)}\right)$$



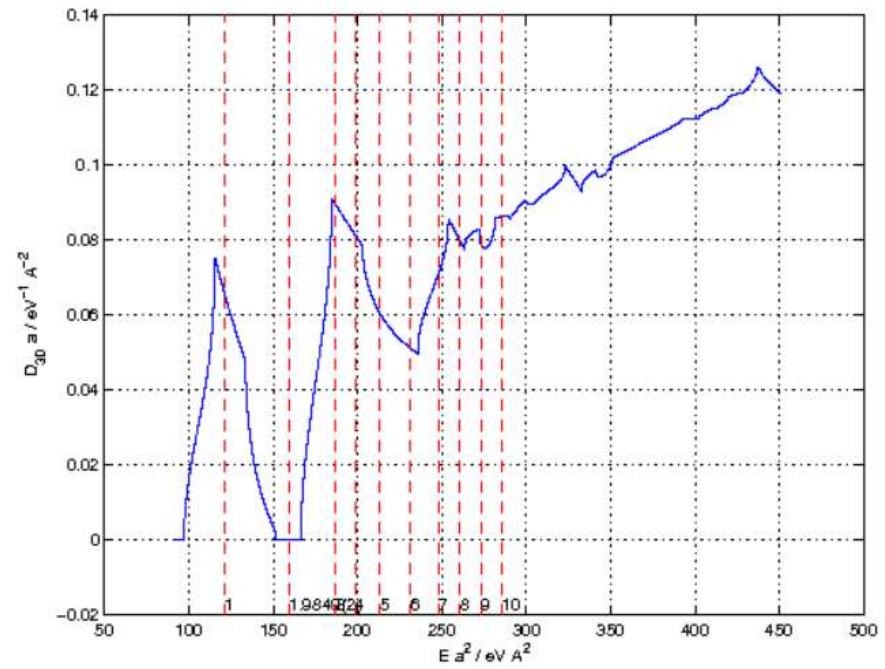
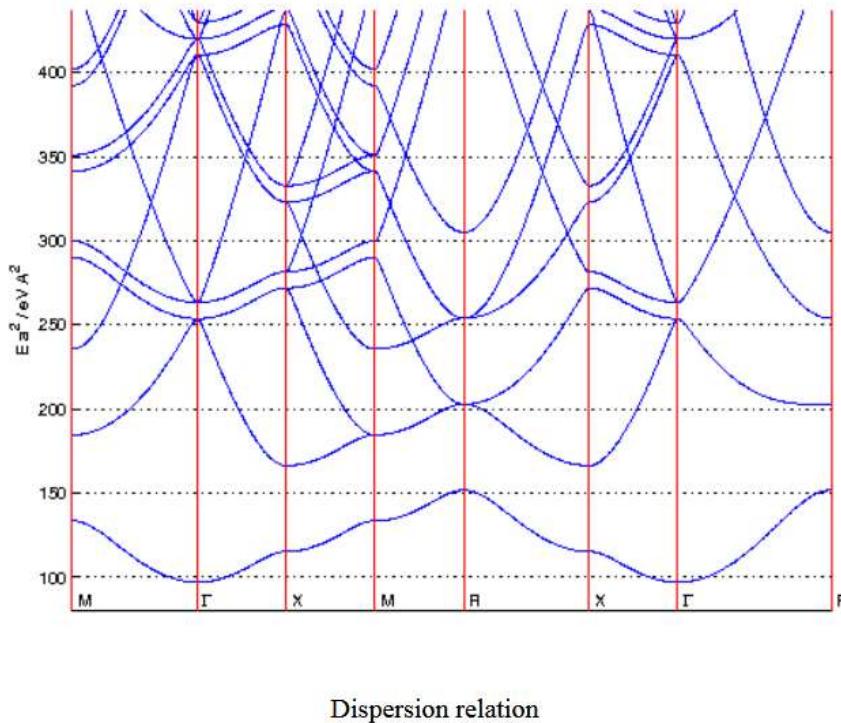
$N_c(300 \text{ K}) =$	2.78E19	1/cm <sup>3</sup>
$N_v(300 \text{ K}) =$	9.84E18	1/cm <sup>3</sup>
$E_g =$	1.166-4.73E-4*T*T/(T+636)	eV
$T_1 =$	50	K
$T_2 =$	1000	K

Semiconductor  
 Si    Ge    GaAs

# metals, semiconductors, and insulators

$$v = 17.024, b = 0.4951, n = 2$$

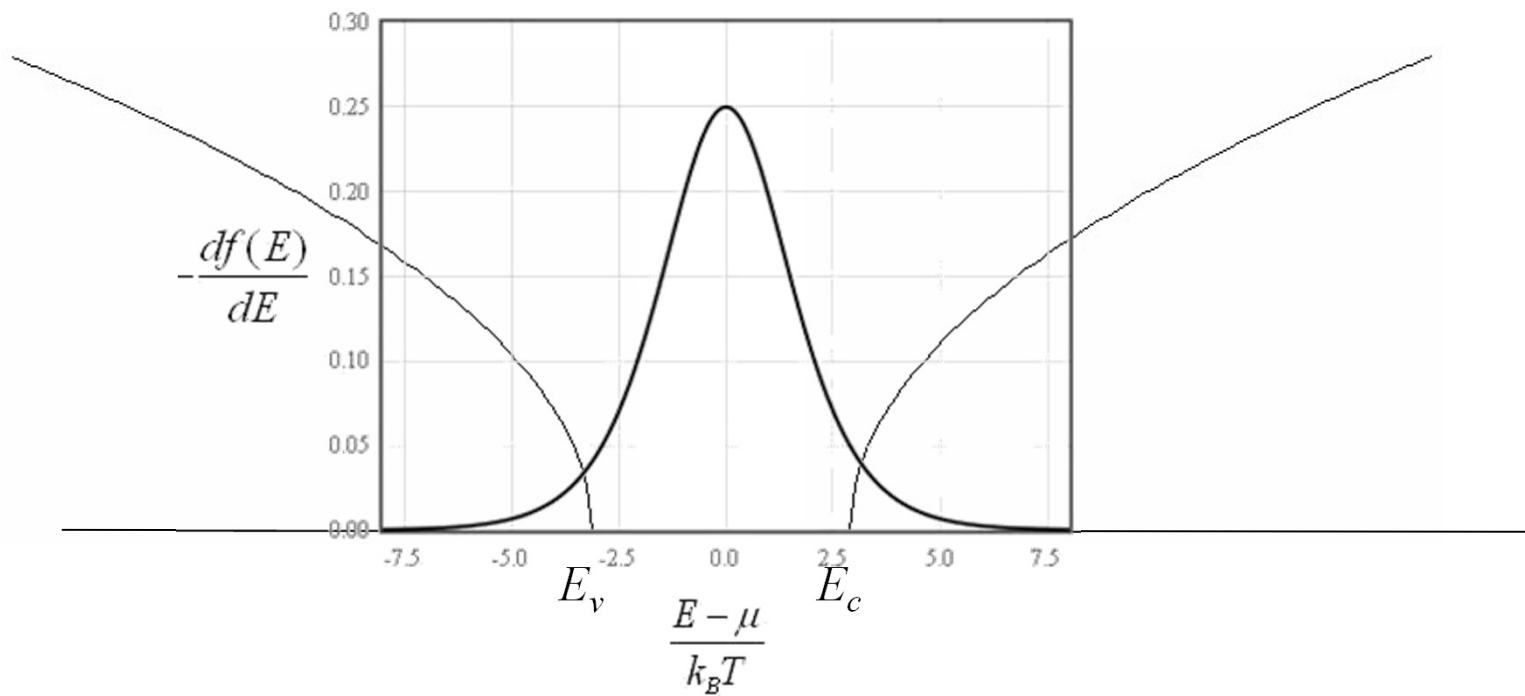
v -- v++ b -- b++ n -- n++



<http://lampx.tugraz.at/~hadley/ss1/separablecrystals/thermo.html>

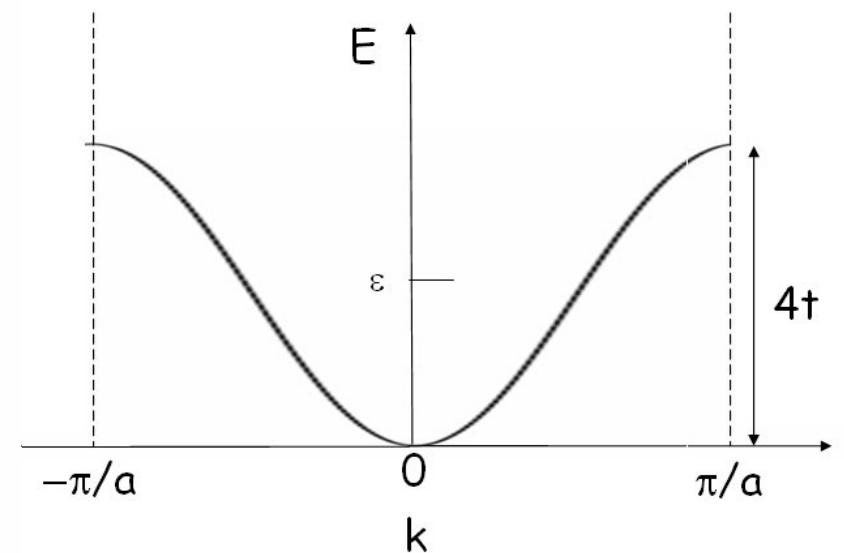
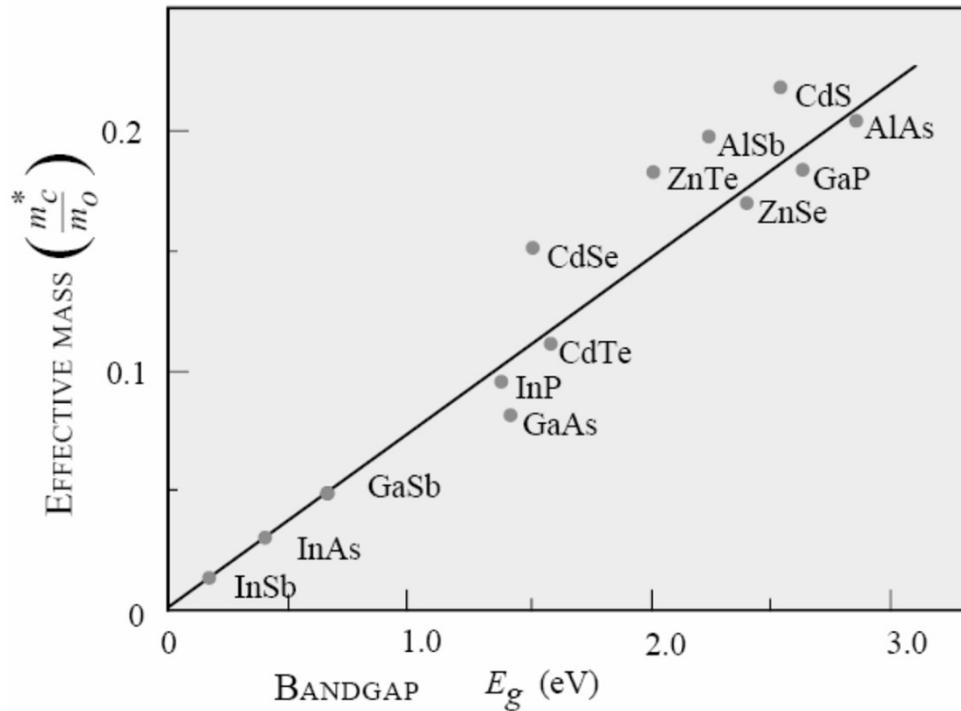
# Narrow bandgap semiconductors

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Use the programs for metals for small bandgap semiconductors.

# Large gap -> large effective mass



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

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

narrow bands -> large effective mass

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

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

# Measuring the effective mass

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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.

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

# Extrinsic Semiconductors

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# Extrinsic semiconductors

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

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

Examples: P, As in Si.

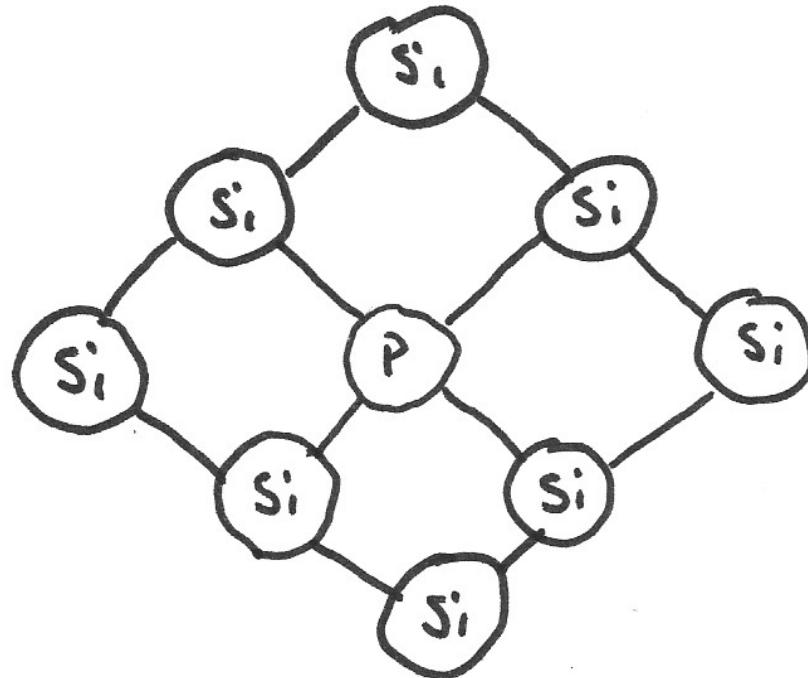
p-type : acceptor atoms contribute holes to the valence band.

Examples: B, Ga, Al in Si.

	IIIA	IVA	VA	VIA
IIB	5 B	6 C	7 N	8 O
	13 Al	14 Si	15 P	16 S
30 Zn	31 Ga	32 Ge	33 As	34 Se
48 Cd	49 In	50 Sn	51 Sb	52 Te

# Ionization of dopants

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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:  $\frac{m^*}{m} \left( \frac{\varepsilon_0}{\varepsilon_r \varepsilon_0} \right)^2$

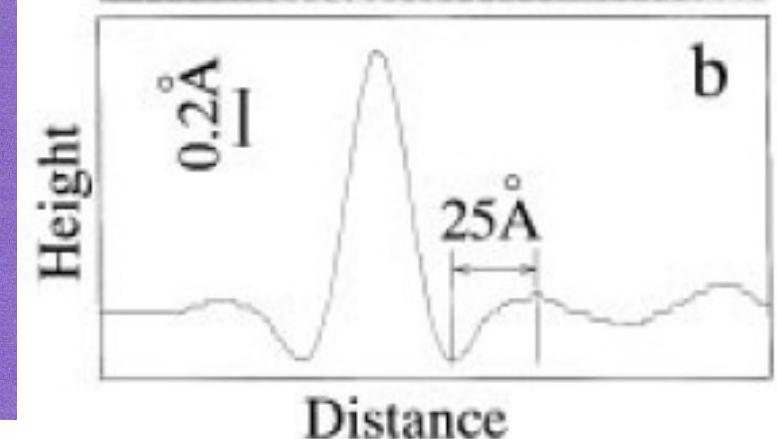
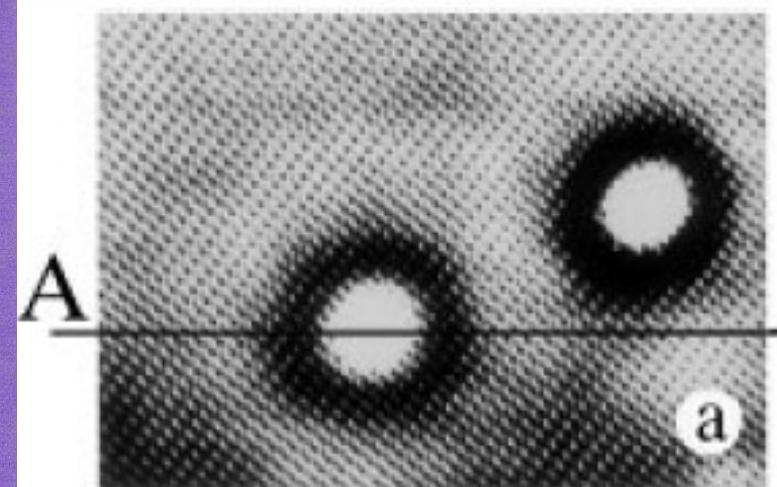
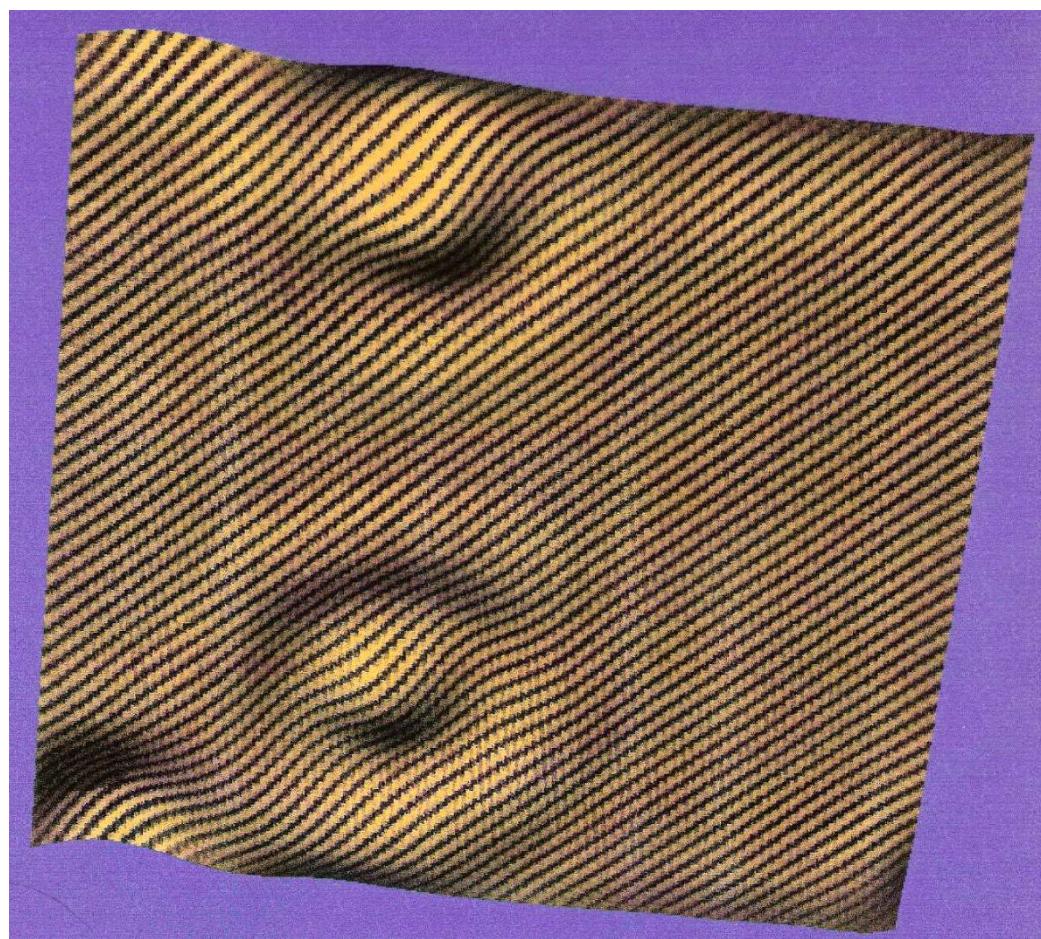
Ionization energy  $\sim 25$  meV

## Direct Observation of Friedel Oscillations around Incorporated $\text{Si}_{\text{Ga}}$ 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

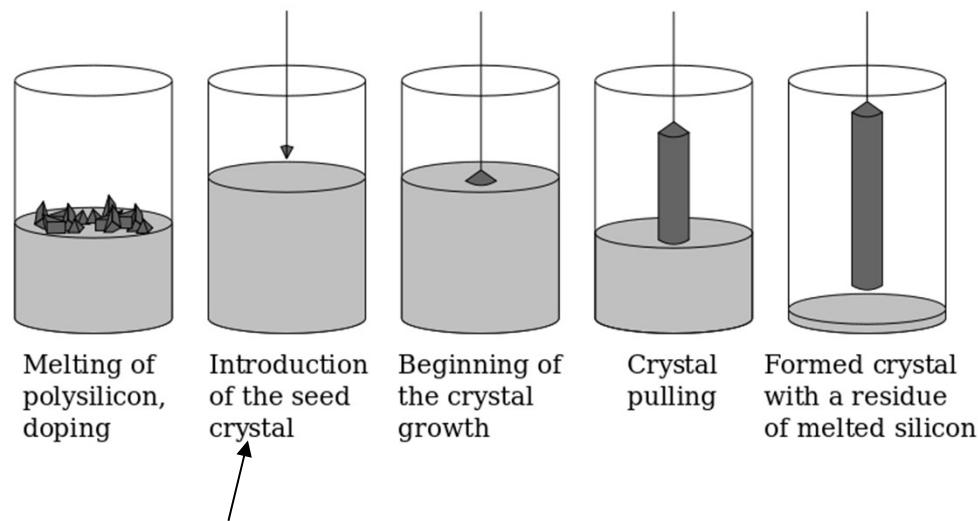
*Research Institute for Materials, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands*

(Received 25 July 1995)



# Crystal growth

## Czochralski Process



images from wikipedia

# Crystal growth

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## Float zone Process

Neutron transmutation

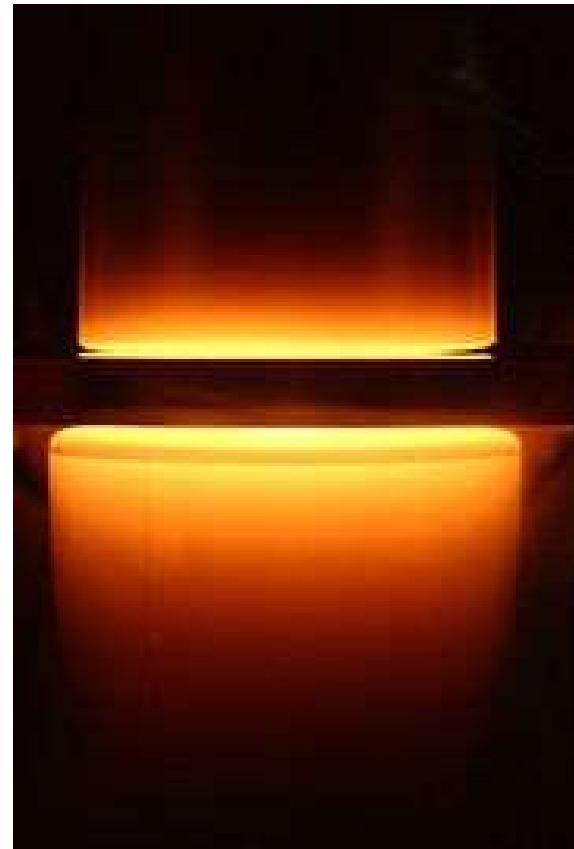
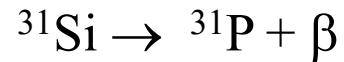
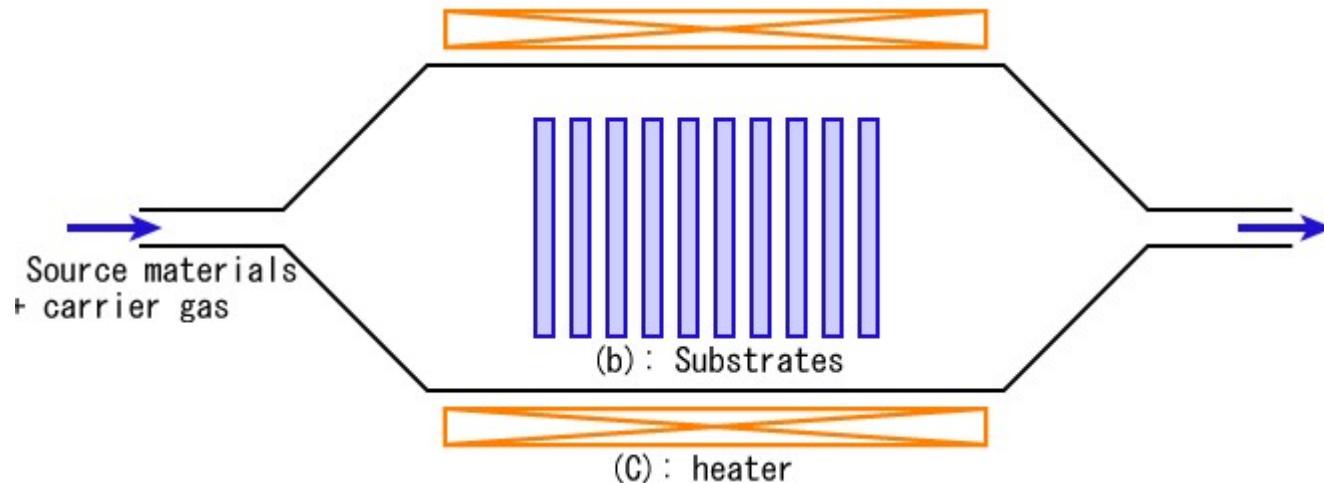


image from wikipedia

# Chemical vapor deposition

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Epitaxial silicon CVD  $\text{SiH}_4$  (silane) or  $\text{SiH}_2\text{Cl}_2$  (dichlorosilane)  
 $\text{PH}_3$  (phosphine) for n-doping or  $\text{B}_2\text{H}_6$  (diborane) for p-doping.

image from wikipedia

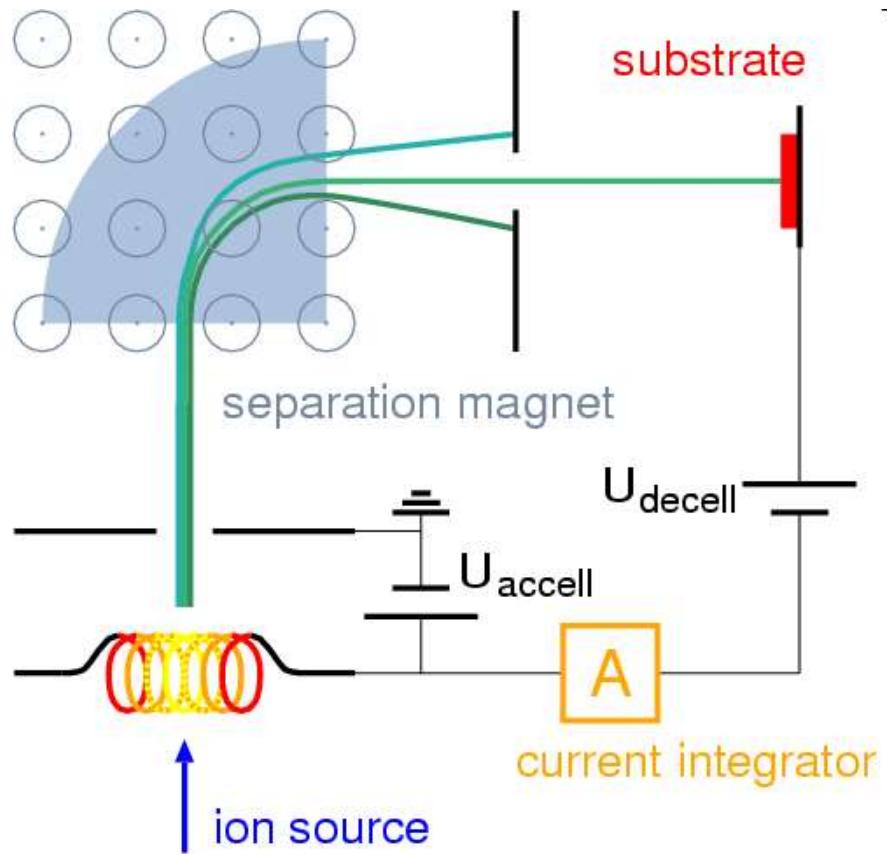
# Gas phase diffusion

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$\text{AsH}_3$  (Arsine) or  $\text{PH}_3$  (phosphine) for n-doping  
 $\text{B}_2\text{H}_6$  (diborane) for p-doping.

# Ion implantation



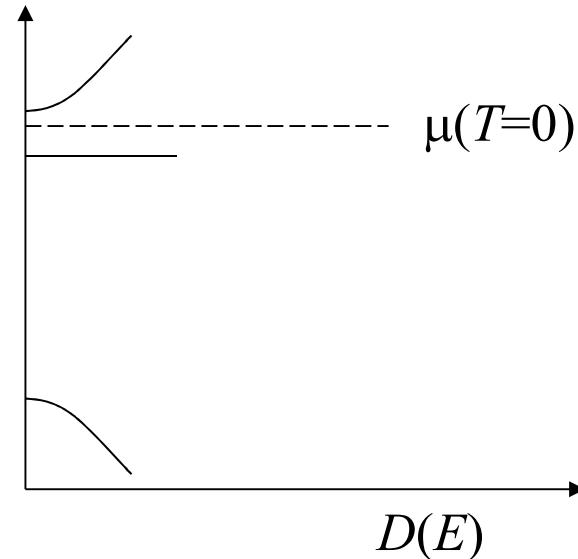
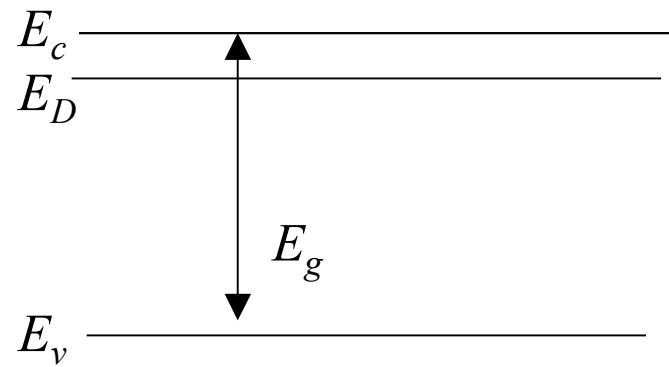
Implant at  $7^\circ$  to avoid channeling

# Donors

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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.

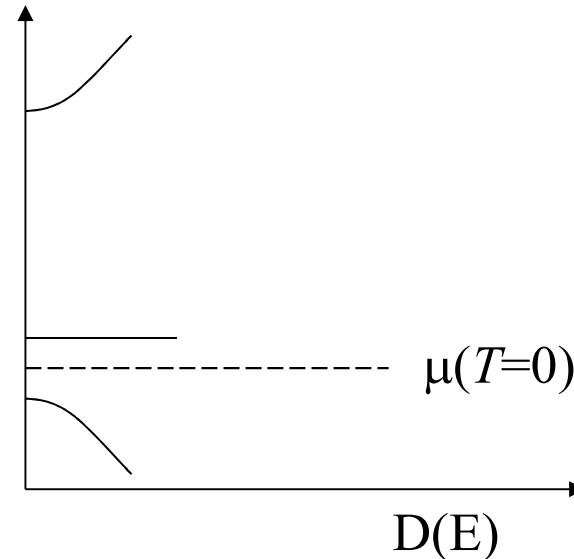
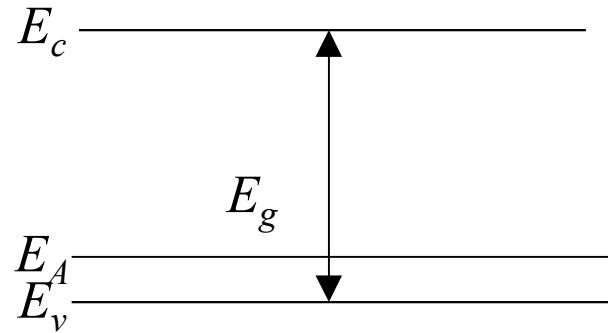
majority carriers: electrons; minority carriers: holes

# Acceptors

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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

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

Energy below the conduction band

Semiconductor	Acceptor	Energy (meV)
Si	B	45
	Al	67
	Ga	72
	In	160
Ge	B	10
	Al	10
	Ga	11
	In	11
GaAs	C	26
	Be	28
	Mg	28
	Si	35

Energy above the valence band

# n-type (extrinsic)

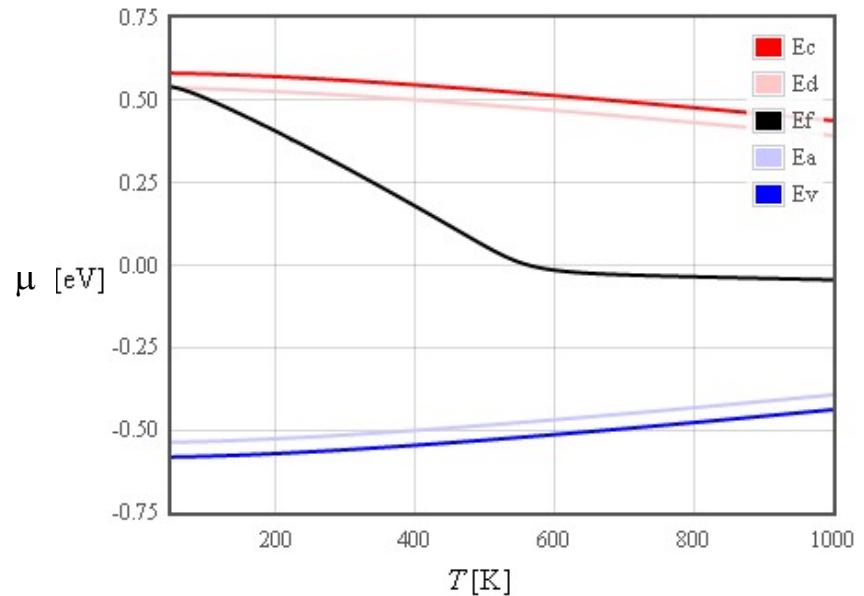
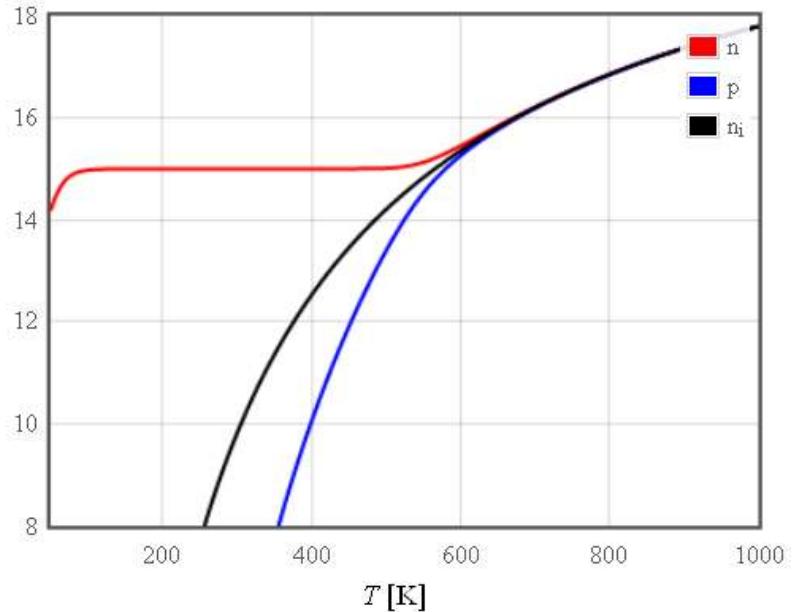
n-type  $N_D > N_A$ ,  $p \sim 0$

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

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

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

$\log_{10} n, p, n_i$   
[cm<sup>-3</sup>]



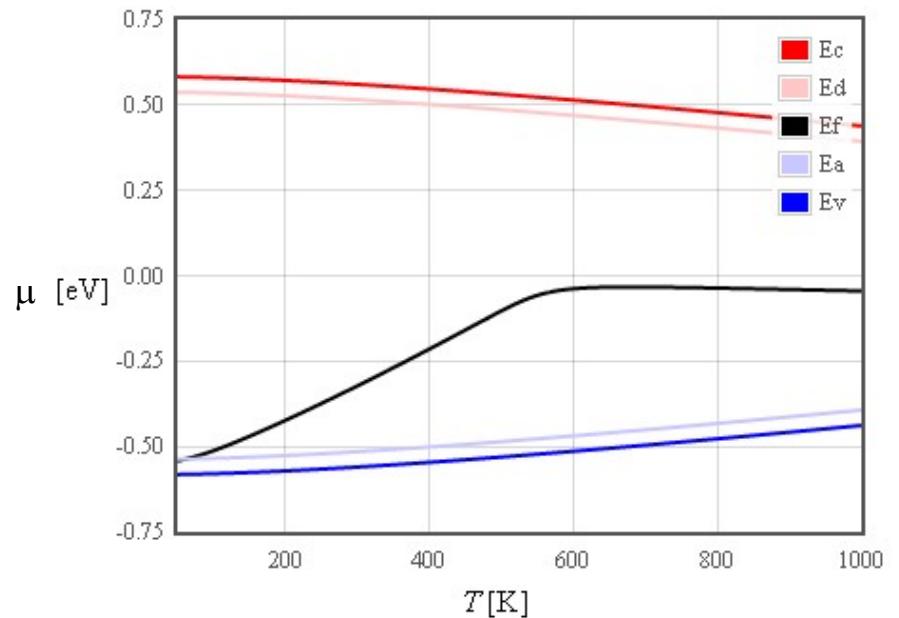
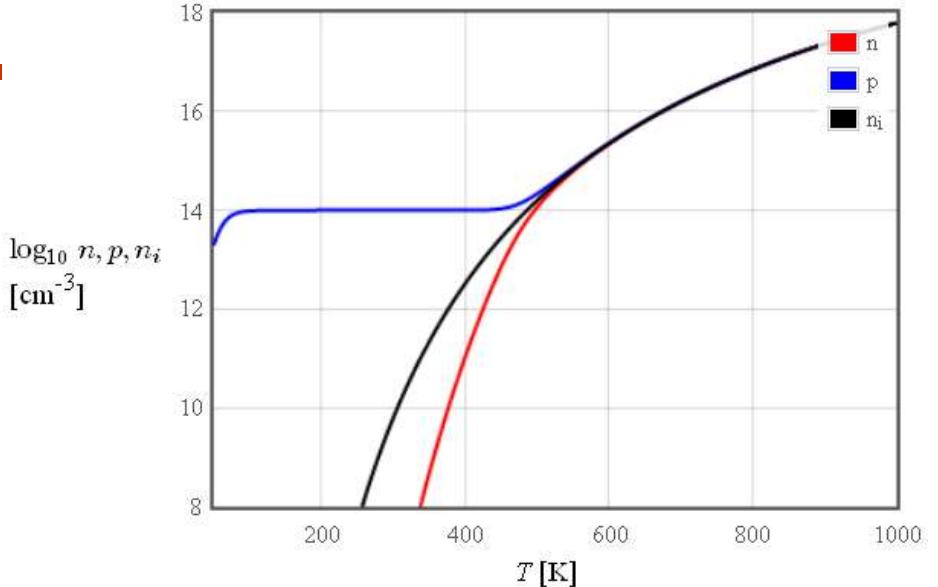
# p-type (extrinsic)

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

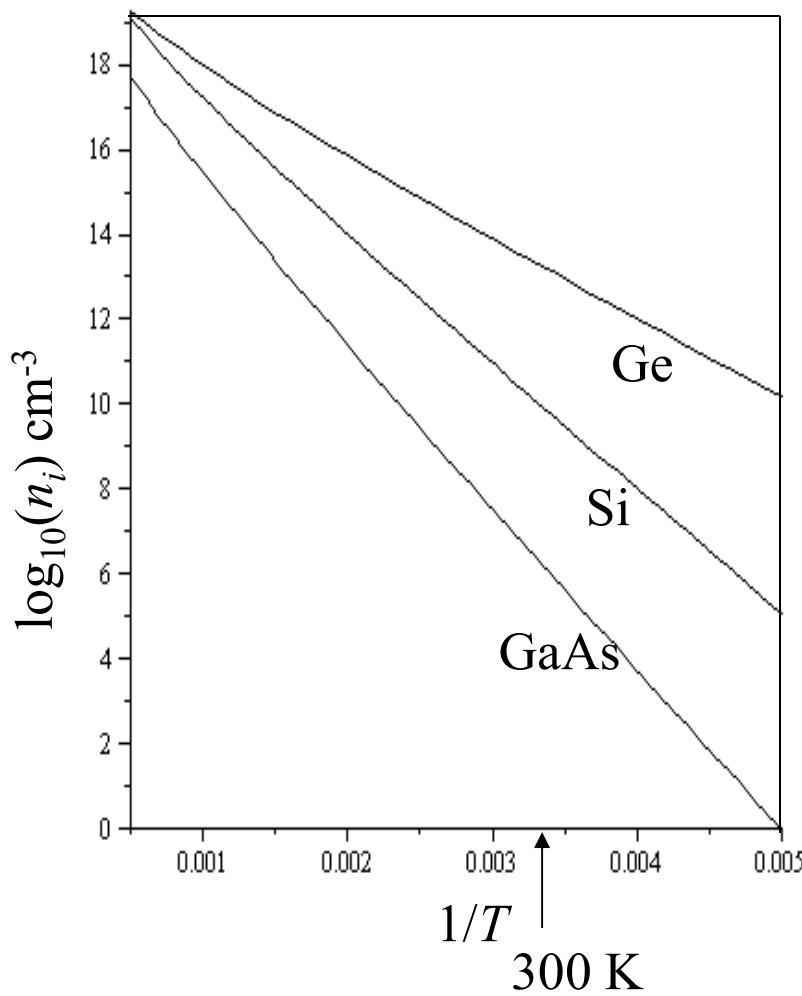
$$p = N_A = N_v \exp\left(\frac{E_v - \mu}{k_B T}\right)$$

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

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

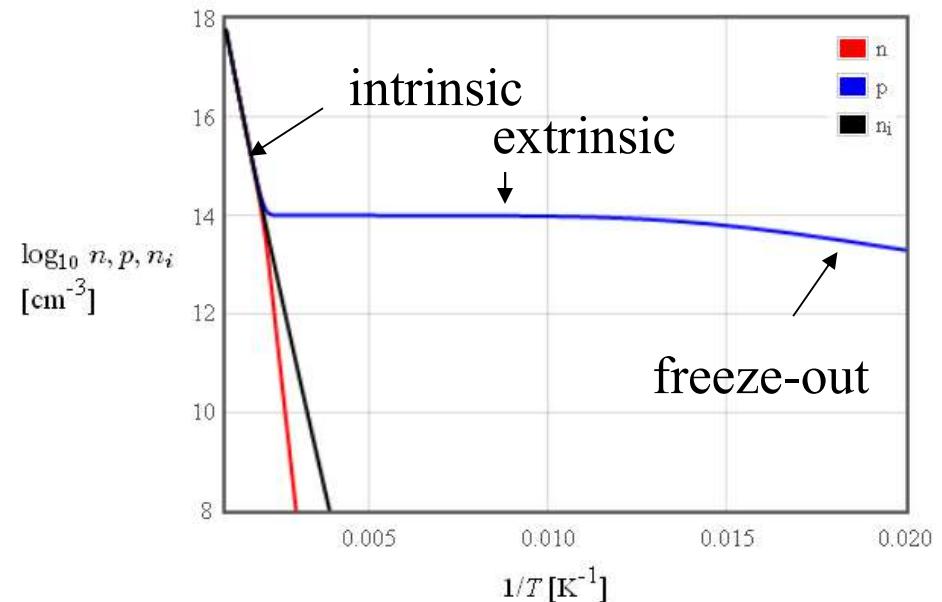


# Intrinsic semiconductors



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

# Extrinsic semiconductors



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

# Ionized donors and acceptors

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For  $E_v + 3k_B T < \mu < E_c - 3k_B T$       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

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

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

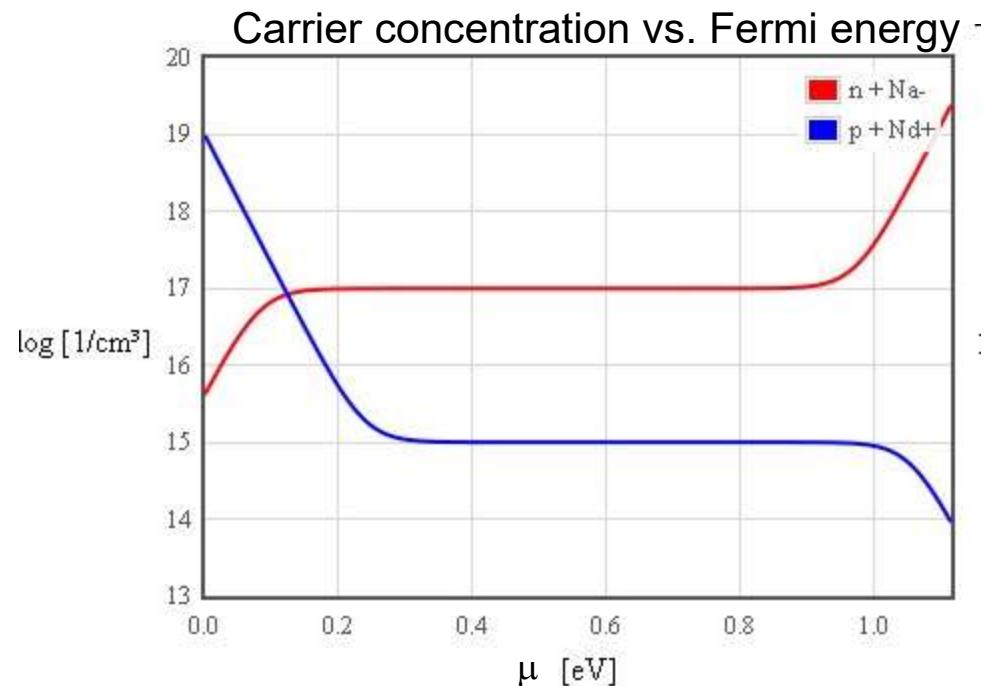
$N_A$  = donor density  $\text{cm}^{-3}$

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

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

# Charge neutrality

$$n + N_A^- = p + N_D^+$$

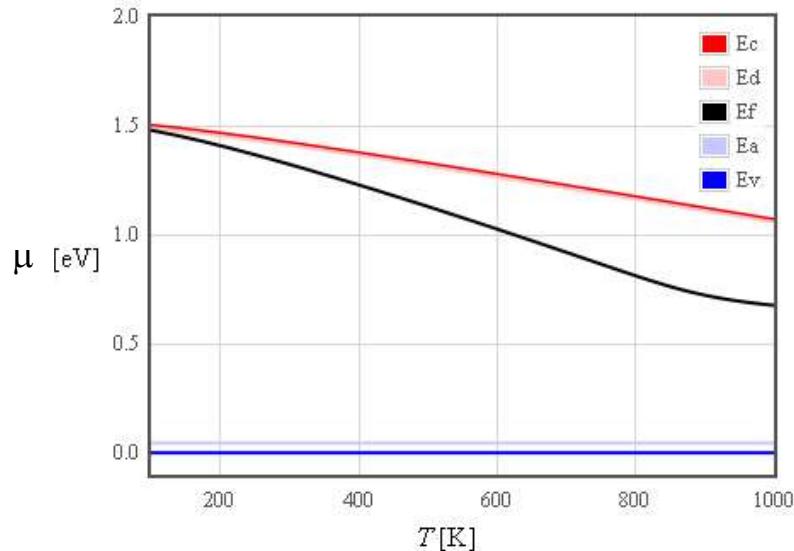


```
for ($i=0; $i<500; $i++) {  
    $Ef = $i*$Eg/500;  
    $n=$Nc*pow($T/300,1.5)*exp(1.6022E-19*($Ef-$Eg)/(1.38E-23*$T));  
    $p=$Nv*pow($T/300,1.5)*exp(1.6022E-19*(-$Ef)/(1.38E-23*$T));  
    $Namin = $Na/(1+4*exp(1.6022E-19*($Ea-$Ef)/(1.38E-23*$T)));  
    $Ndplus = $Nd/(1+2*exp(1.6022E-19*($Ef-$Ed)/(1.38E-23*$T)));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

E <sub>f</sub>	n	p	N <sub>d</sub> <sup>+</sup>	N <sub>a</sub> <sup>-</sup>	log(n+N <sub>a</sub> <sup>-</sup> )	log(p+N <sub>d</sub> <sup>+</sup> )
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
0.00896	5.88210450791	6.95555002157E+18	1E+15	5.925500025E+15	15.7760078057	18.8404521605

## 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.



$N_c(300 \text{ K}) = 4.45\text{E}17$	1/cm <sup>3</sup>	Semiconductor
$N_v(300 \text{ K}) = 7.72\text{E}18$	1/cm <sup>3</sup>	Si    Ge    GeAs
$E_g = 1.519 - 5.41 \times 10^{-4} T^2 / (T + 204)$	eV	
$N_d = 1\text{E}16$	1/cm <sup>3</sup>	Donor
$E_c - E_d = 0.012$	eV	P in Si    P in Ge    Si in GaAs
$N_a = 1\text{E}12$	1/cm <sup>3</sup>	Acceptor
$E_a - E_v = 0.045$	eV	B in Si    B in Ge    Si in GaAs
$T_1 = 100$	K	
$T_2 = 1000$	K	
<input type="button" value="Replot"/>		

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  $n_i = \sqrt{N_c \left( \frac{T}{300} \right)^{3/2} N_v \left( \frac{T}{300} \right)^{3/2}} \exp \left( \frac{-E_g}{2k_B T} \right)$ .

