

# 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.

# n and p

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The electron density and hole density are:

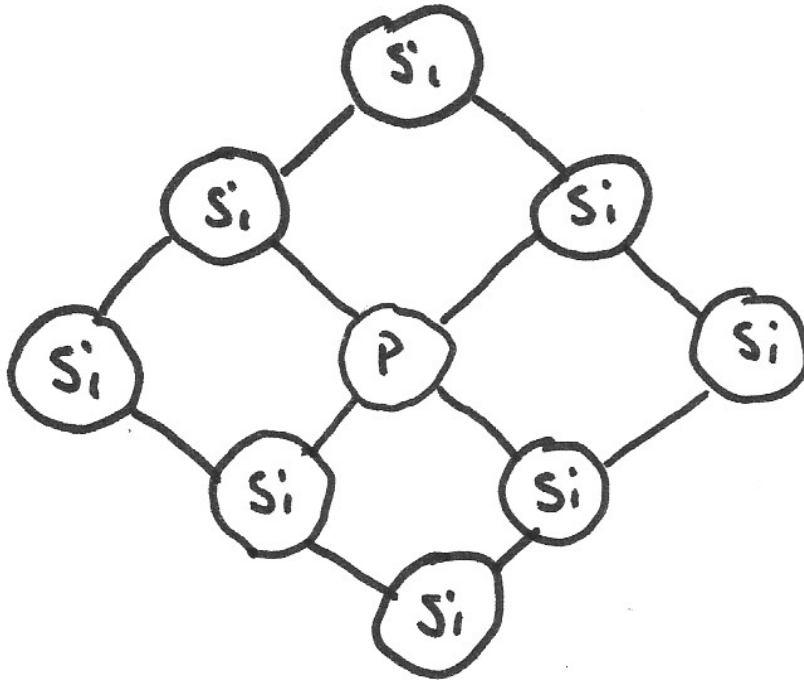
$$n = N_c \exp\left(\frac{E_F - E_c}{k_B T}\right) \quad p = N_v \exp\left(\frac{E_v - E_F}{k_B T}\right)$$

The law of mass action:

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

# Ionization of dopants

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

$$E_n = -\frac{me^4}{8\epsilon_0^2 h^2 n^2}$$

Ionization energy is smaller by a factor:

$$\frac{m^*}{m} \left( \frac{\epsilon_0}{\epsilon_r \epsilon_0} \right)^2$$

Ionization energy  $\sim 25$  meV

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

acceptors in Si



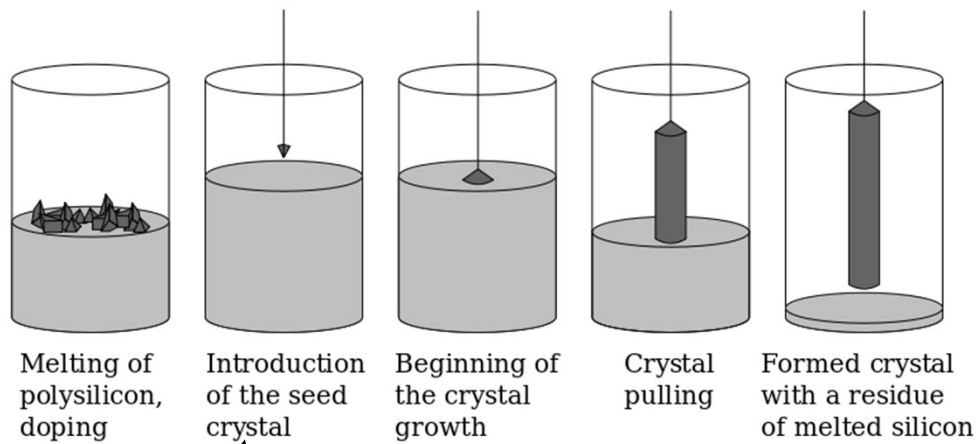
donors in Si



# Crystal growth

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## Czochralski Process



add dopants to the melt



images from wikipedia

# Crystal growth

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## Float zone Process

Neutron transmutation

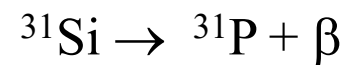
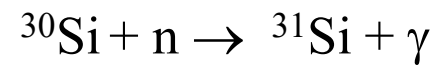


image from wikipedia

# Gas phase diffusion

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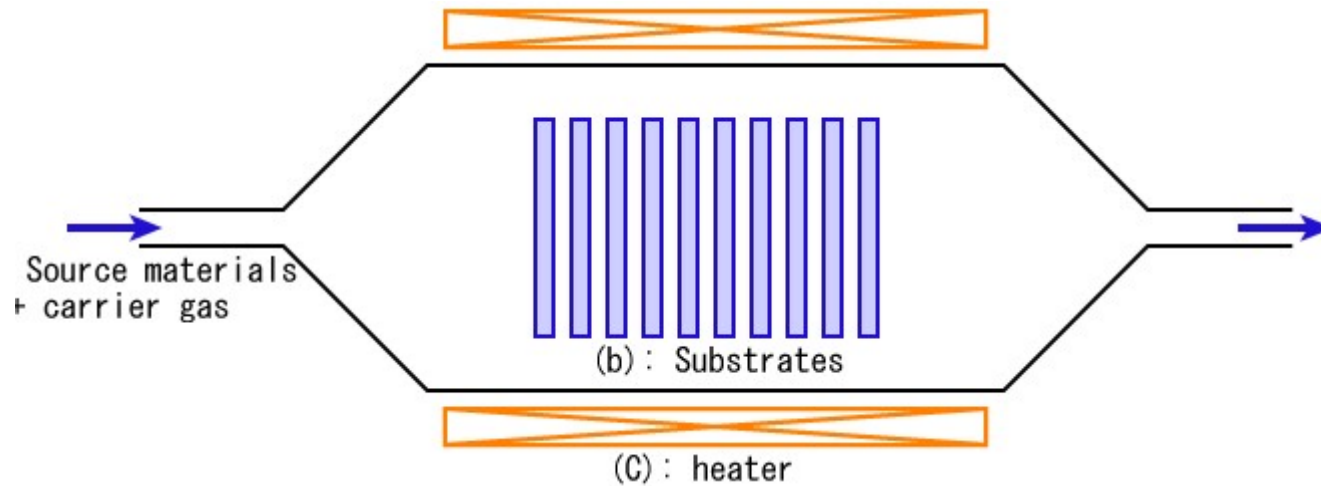


$\text{AsH}_3$  (Arsine) or  $\text{PH}_3$  (phosphine) for n-doping  
 $\text{B}_2\text{H}_6$  (diborane) for p-doping.



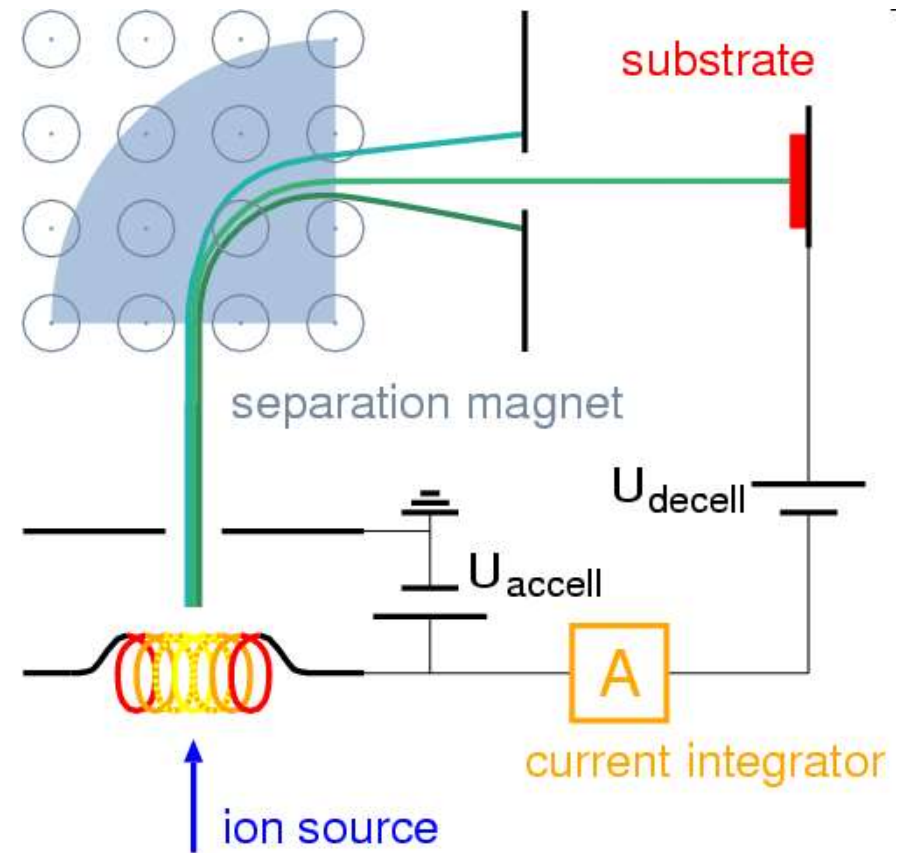
# Chemical vapor deposition

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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.

# Ion implantation



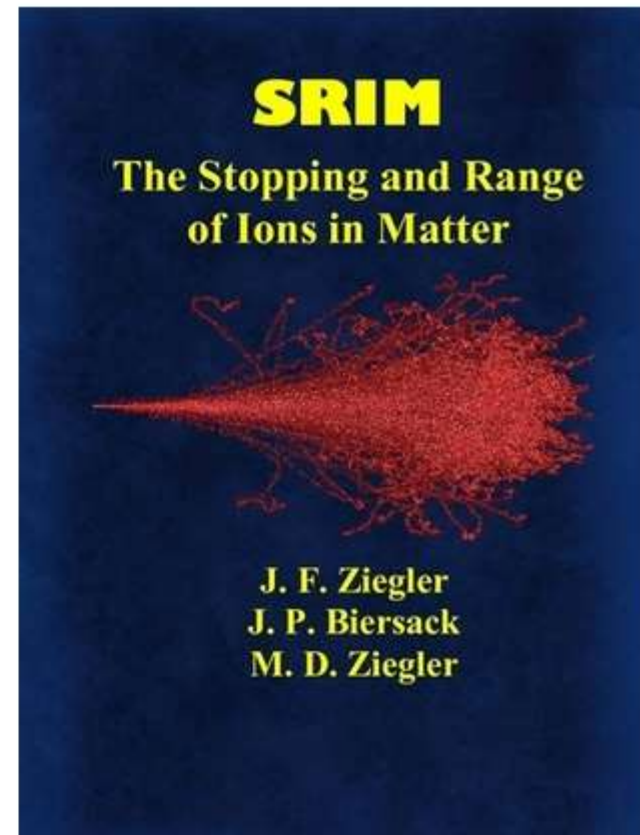
Implant at  $7^\circ$  to avoid channeling

# *SRIM*

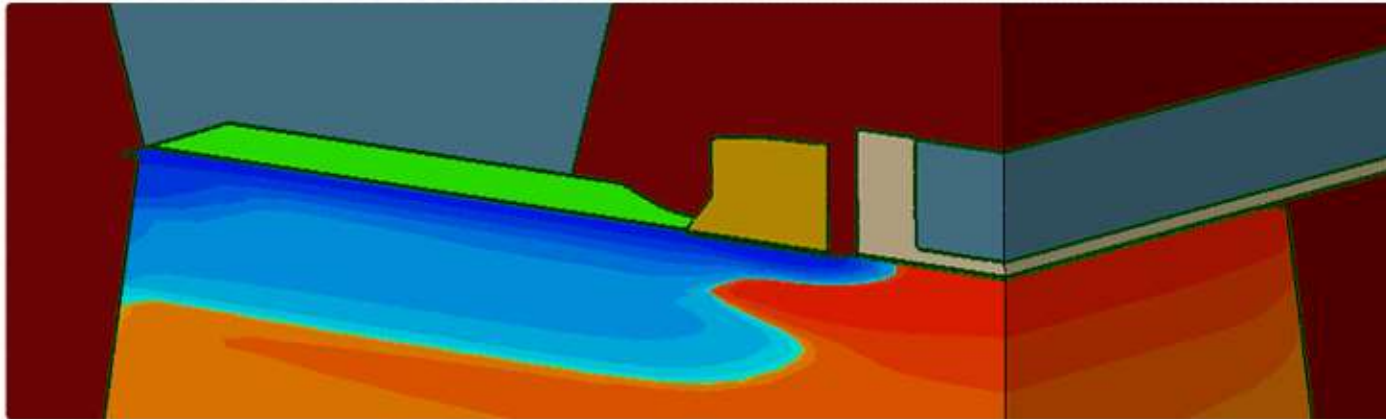
## *The Stopping and Range of Ions in Matter*

*James F. Ziegler, Jochen P. Biersack, Matthias D. Ziegler*

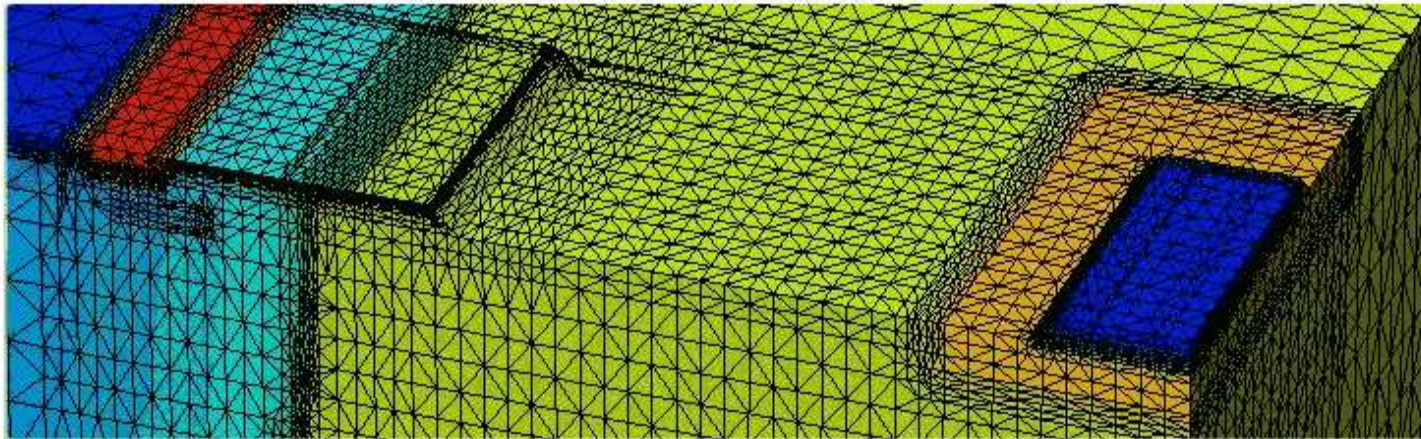
- Ch 1 - **Historical Review**
- Ch 2 - **Nuclear Stopping of Ions**
- Ch 3 - **Electronic Stopping of Ions**
- Ch 4 - **Stopping of Energetic Light Ions**
- Ch 5 - **Stopping of Ions in Compounds**
- Ch 6 - **Ion Straggling**
- Ch 7 - **TRIM : Scientific Background**
- Ch 8 - **TRIM : Setup and Input**
- Ch 9 - **TRIM : Output Files**
- Ch 10 - **Stopping and Range Tables**
- Ch 11 - **SRIM Tutorials**



## Process Simulation



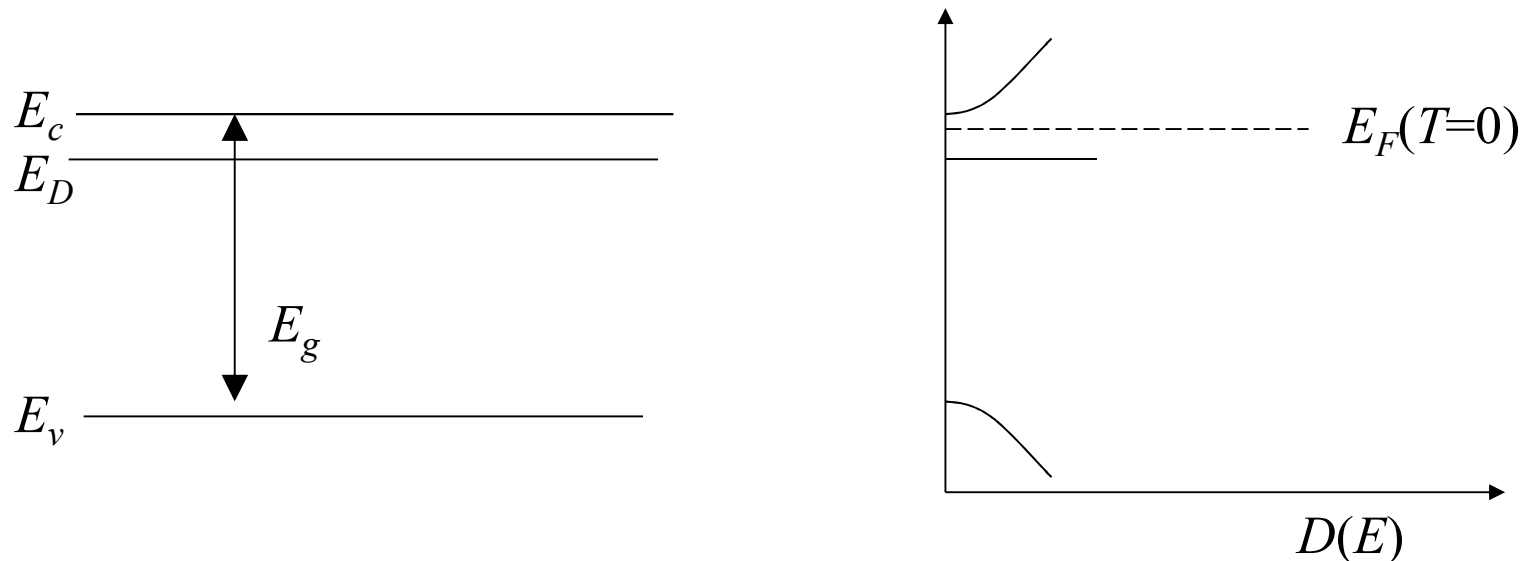
## Device Simulation



# Donors

Five valence electrons: P, As

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



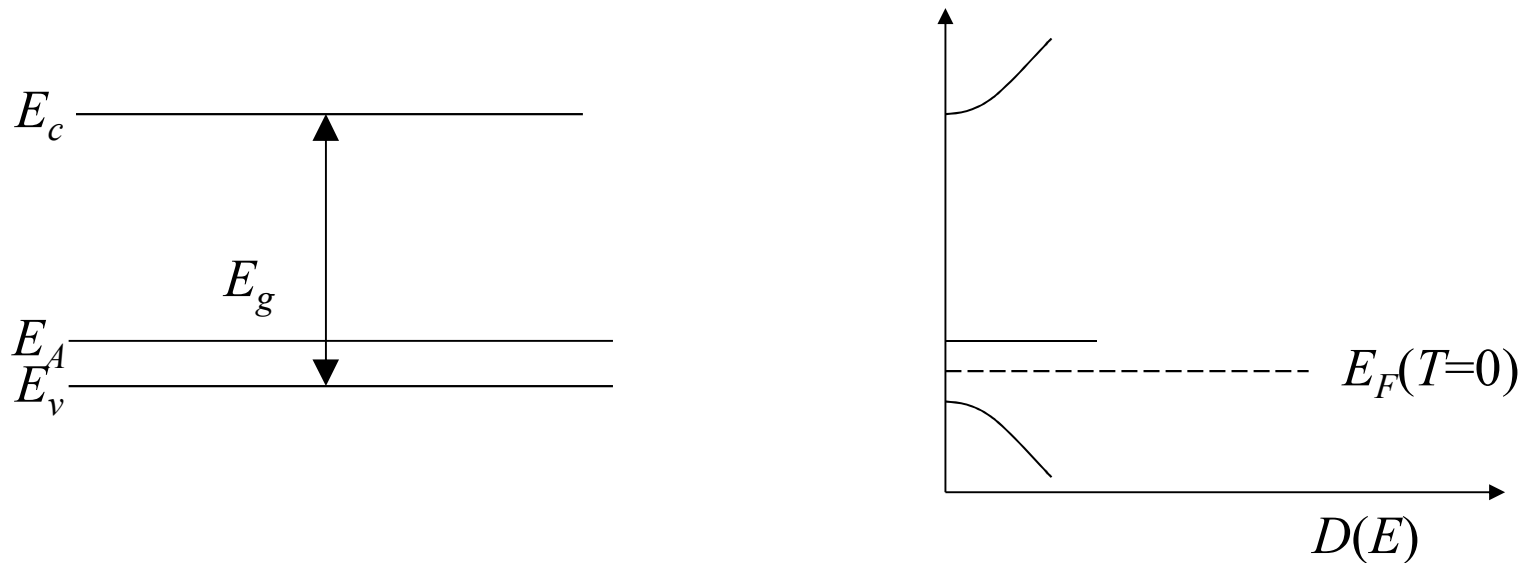
n-type:  $n \sim N_D$  Many more electrons in the conduction band than holes in the valence band.

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

# 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

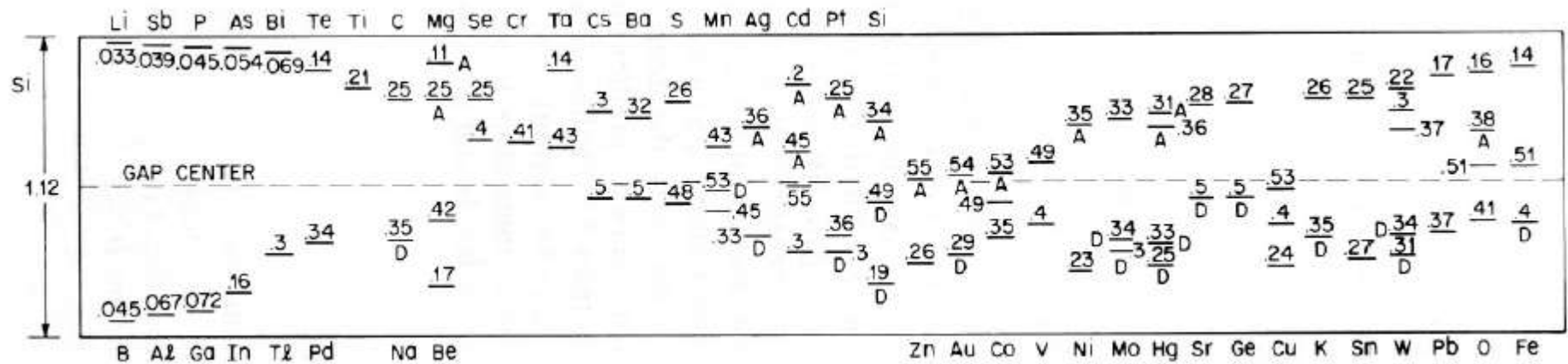
Energy below the conduction band



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





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

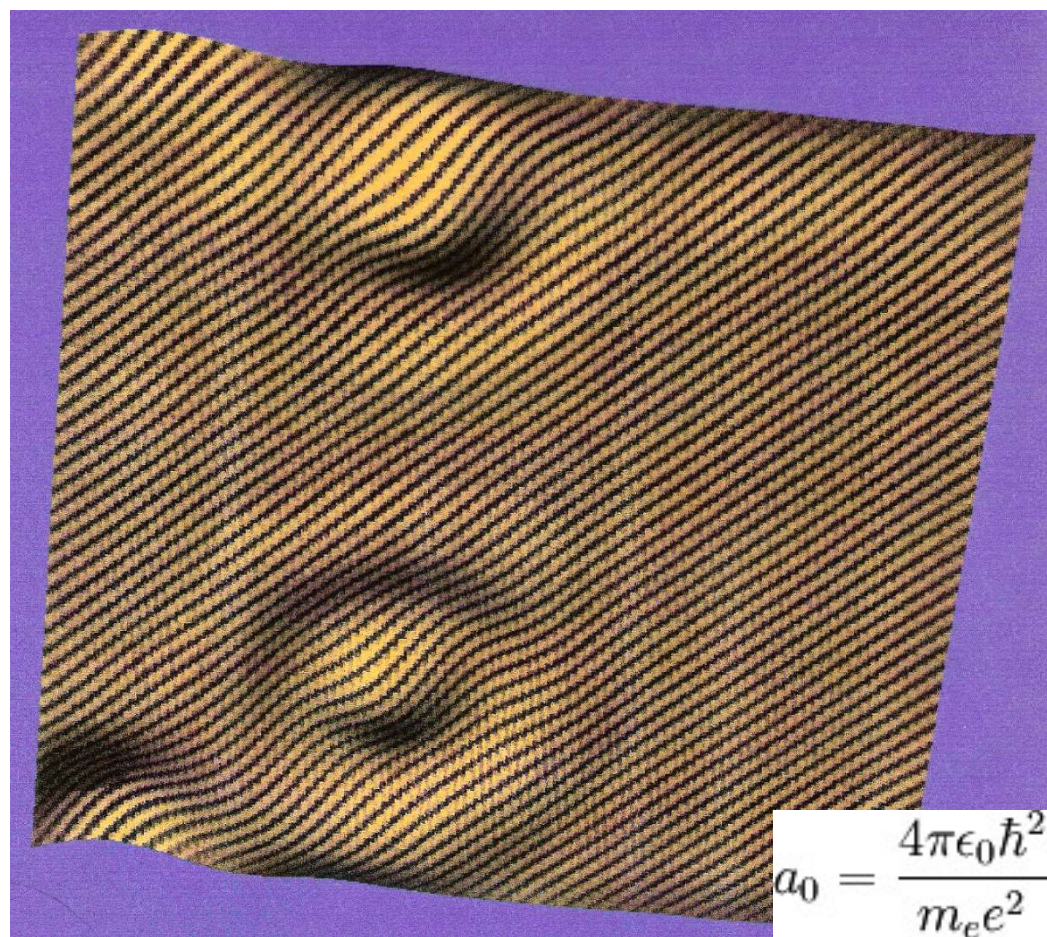


## Direct Observation of Friedel Oscillations around Incorporated $\text{Si}_{\text{Ga}}$ Dopants in GaAs by Low-Temperature Scanning Tunneling Microscopy

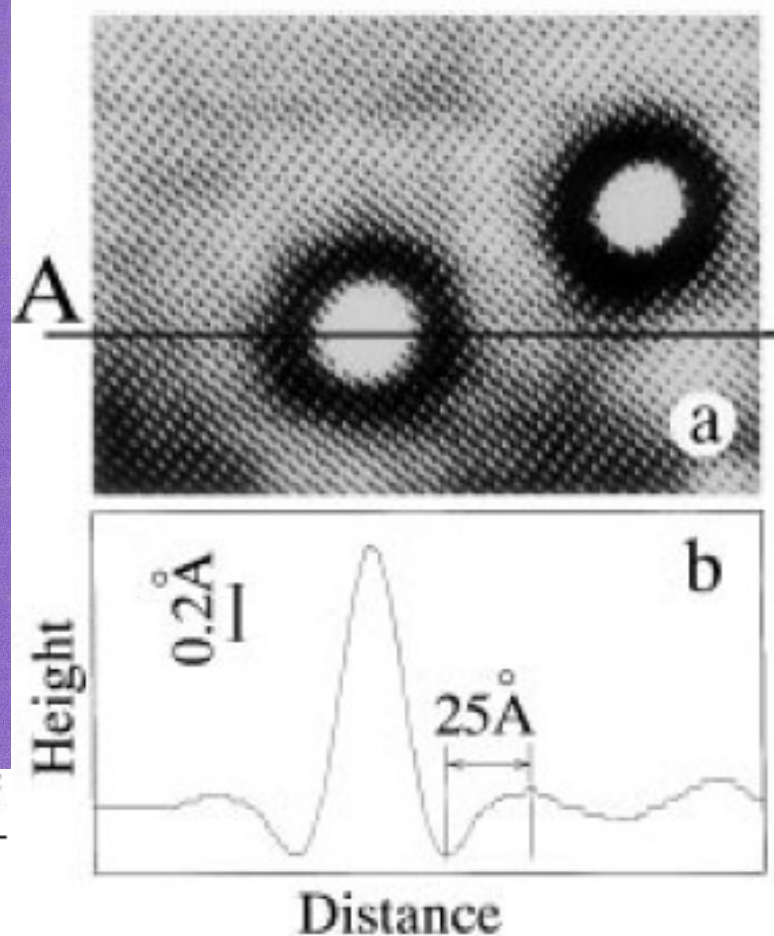
M. C. M. M. van der Wielen, A. J. A. van Roij, and H. van Kempen

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

(Received 25 July 1995)

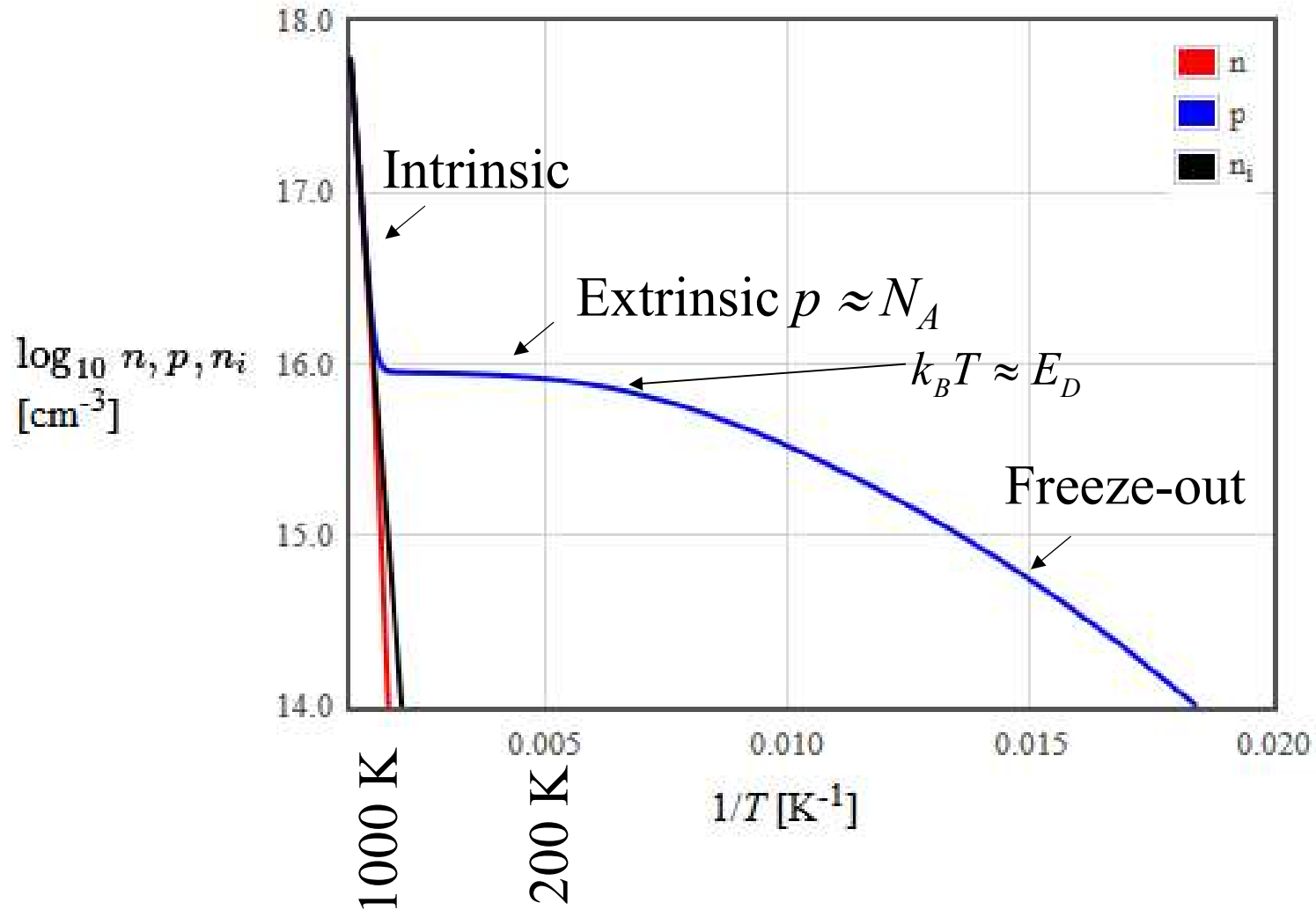


$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$$



# Temperature dependence

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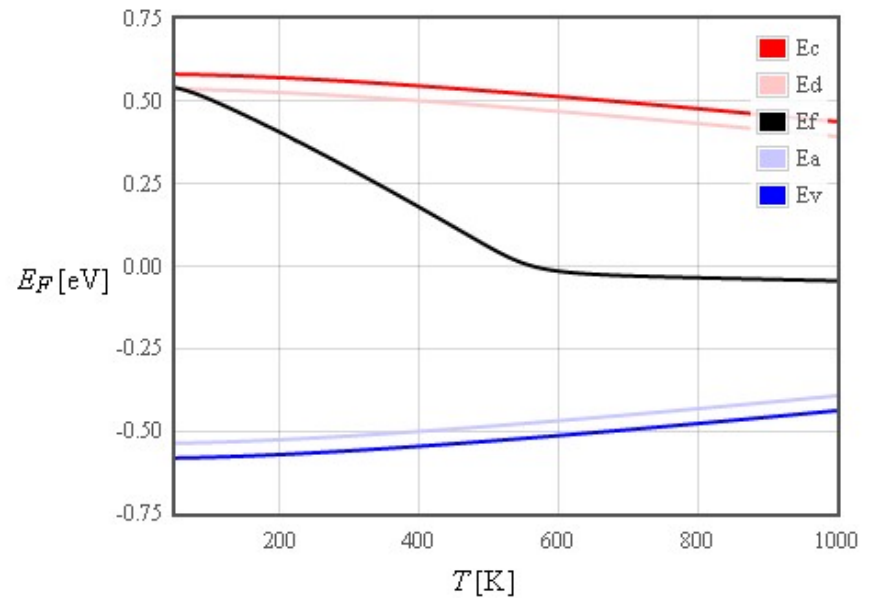
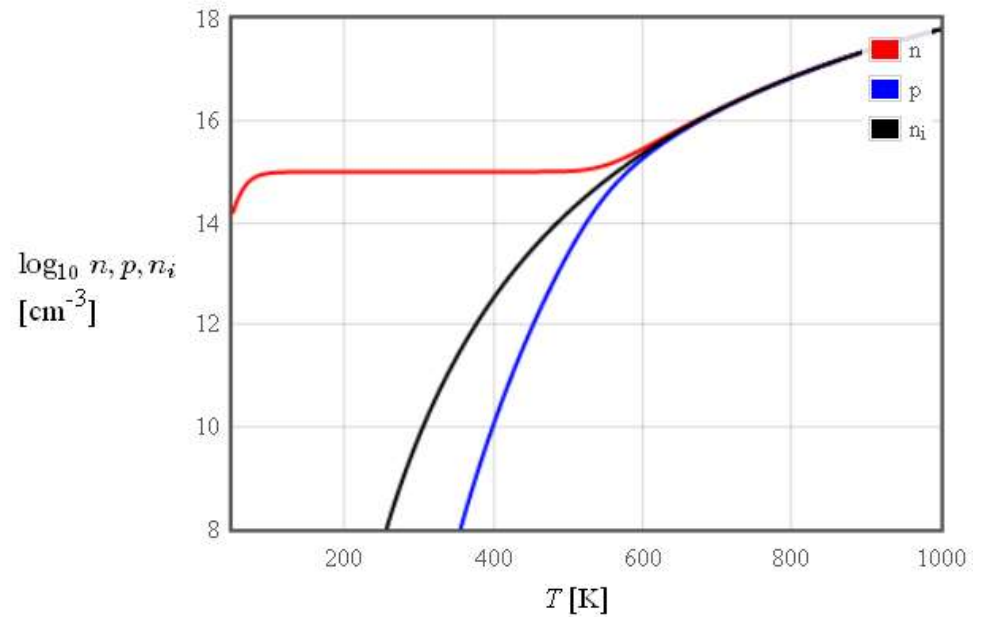


# n-type (extrinsic)

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

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

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

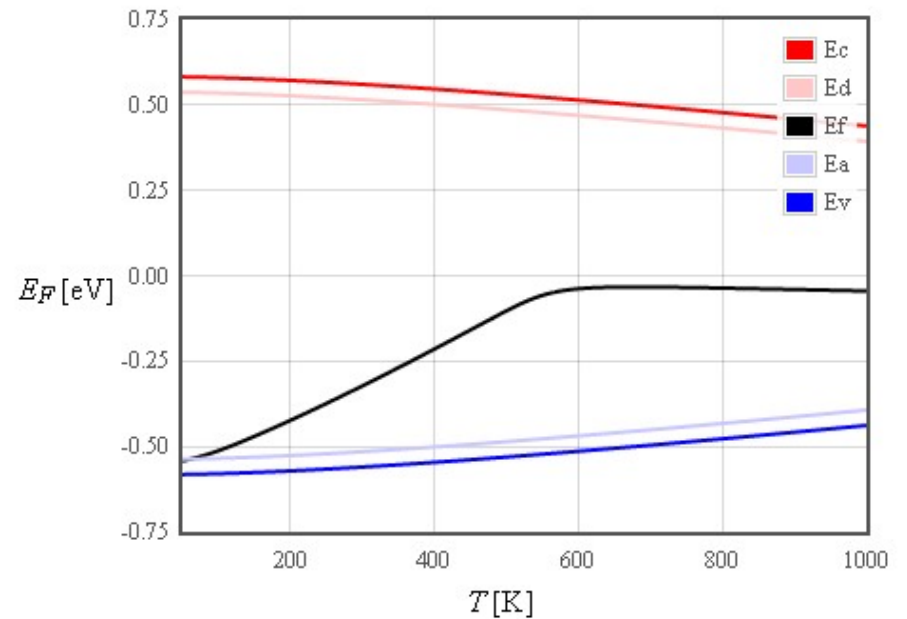
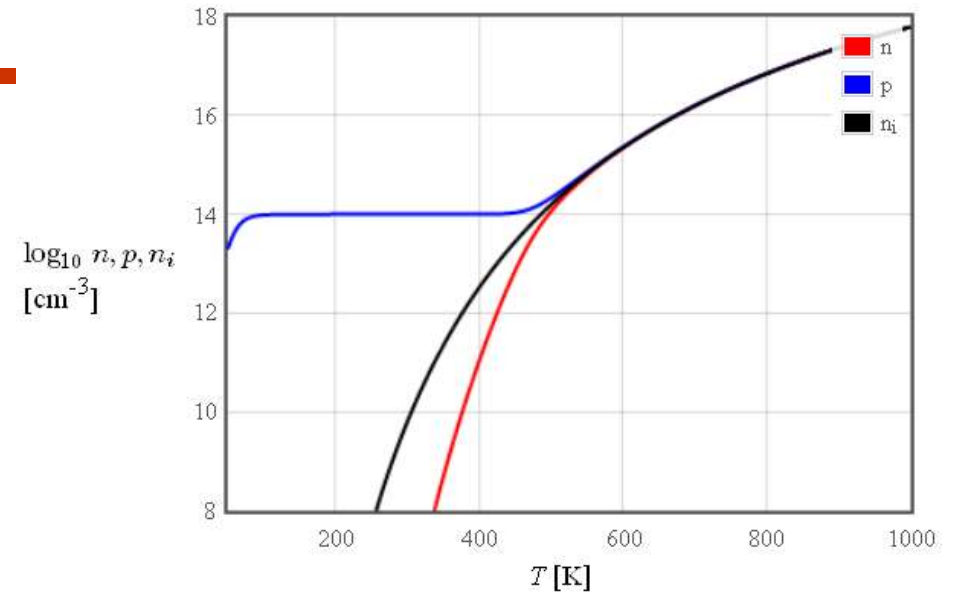


# p-type (extrinsic)

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

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

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



# Intrinsic / Extrinsic

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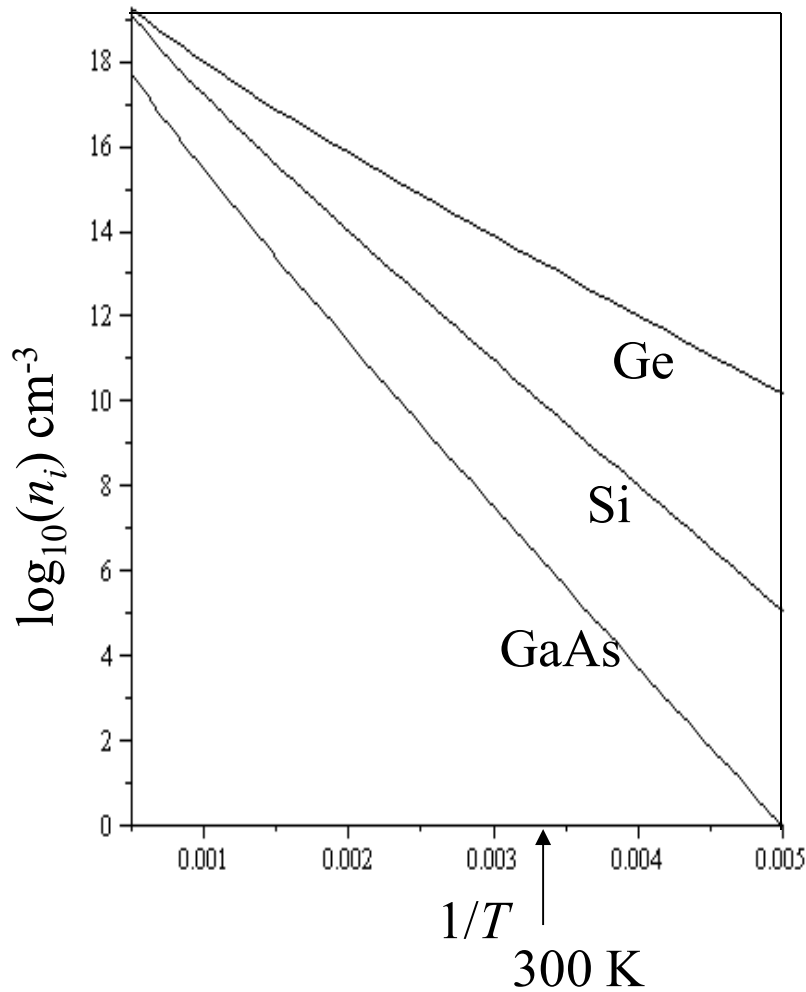
Intrinsic:  $n = p$

Conductivity strongly temperature dependent near room temperature

Extrinsic:  $n \neq p$

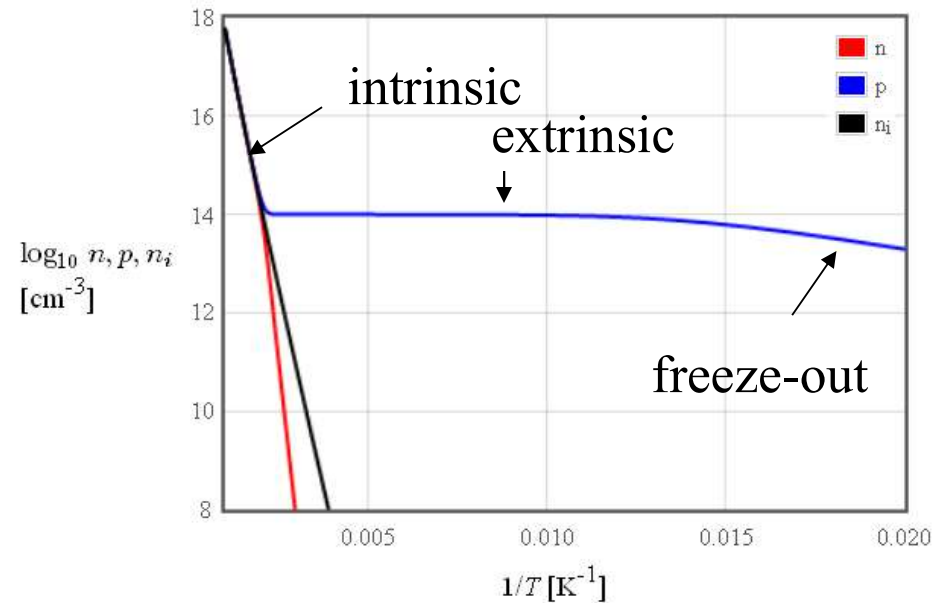
Conductivity almost temperature independent at room temperature

# 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  $E_v + 3k_B T < E_F < E_c - 3k_B T$  Boltzmann approximation

$$N_D^+ = \frac{N_D}{1 + 2 \exp\left(\frac{E_F - E_D}{k_B T}\right)} \qquad N_A^- = \frac{N_A}{1 + 4 \exp\left(\frac{E_A - E_F}{k_B T}\right)}$$

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

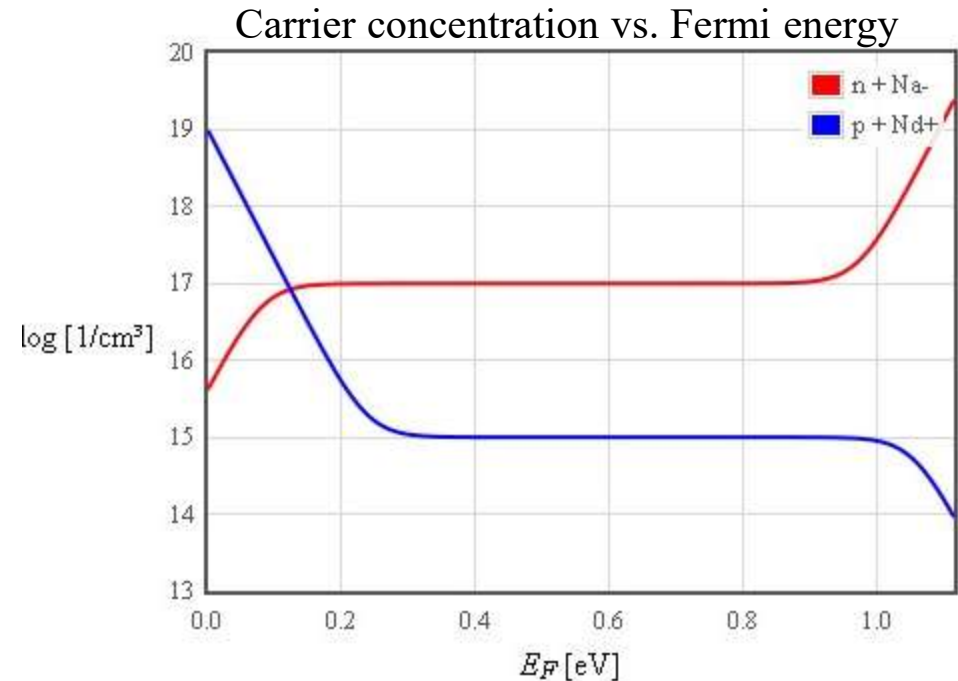
$N_D$  = donor density  $\text{cm}^{-3}$        $N_D^+$  = ionized donor density  $\text{cm}^{-3}$

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

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

# Charge neutrality

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



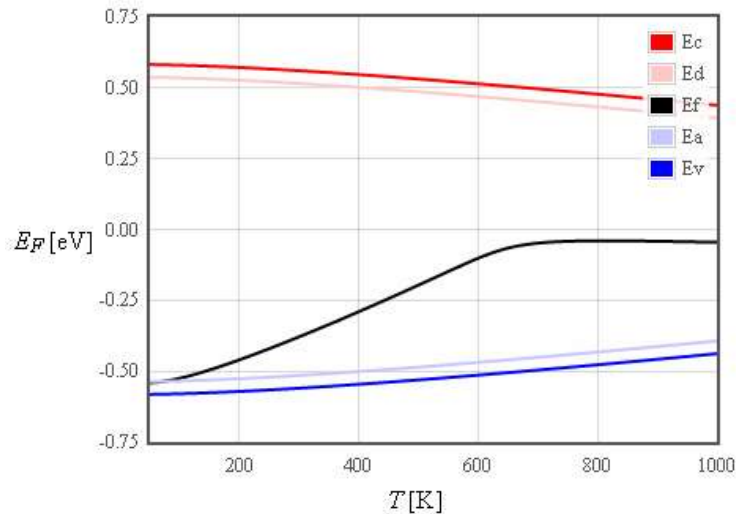
```

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)));
}
    
```

$E_f$	$n$	$p$	$N_d^+$	$N_a^-$	$\log(n+N_a^-)$	$\log(p+N_d^+)$
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	5.89210460791	6.95665026215E+18	1E+15	5.8256000025E+15	15.7660076057	18.8404621605



# Calculating $E_F(T)$ numerically



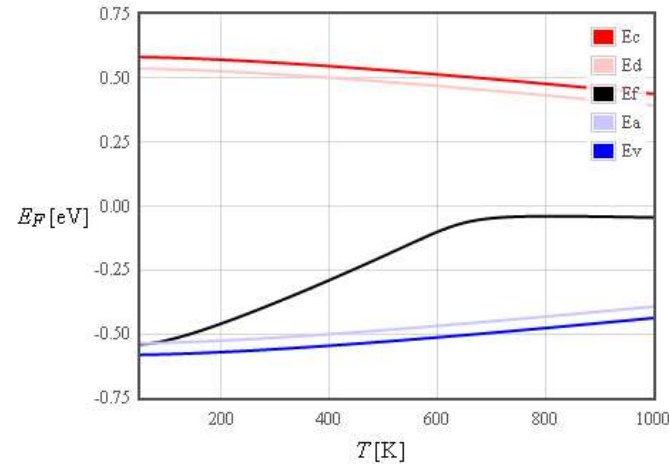
$N_c(300\text{ K}) = 2.78\text{E}19$	1/cm <sup>3</sup>	Semiconductor
$N_v(300\text{ K}) = 9.84\text{E}18$	1/cm <sup>3</sup>	
$E_g = 1.166 - 4.73\text{E-}4 * T * T / (T + 636)$	eV	<input type="button" value="Si"/> <input type="button" value="Ge"/> <input type="button" value="GaAs"/>
$N_d = 1\text{E}15$	1/cm <sup>3</sup>	Donor
$E_c - E_d = 0.045$	eV	
$N_a = 1\text{E}16$	1/cm <sup>3</sup>	Acceptor
$E_a - E_v = 0.045$	eV	
$T_1 = 50$	K	<input type="button" value="B in Si"/> <input type="button" value="B in Ge"/> <input type="button" value="Si in GaAs"/>
$T_2 = 1000$	K	
<input type="button" value="Replot"/>		

[Source code](#)

$E_f$	$n$	$p$	$N_d^+$	$N_a^-$	$T$
0.0421442489848	2.40151024146E-36	1.42005993475E+16	1E+15	1.52148150693E+16	100
0.0432605499091	3.55188567934E-34	1.60496732529E+16	1E+15	1.70727565871E+16	104
0.0443992886238	3.6447725184E-32	1.79708501904E+16	1E+15	1.89867455992E+16	108
0.0455696761919	2.70091324524E-30	1.99342913907E+16	1E+15	2.0961617146E+16	112
0.046759290261	1.49291303432E-28	2.19530074854E+16	1E+15	2.29663635196E+16	116
0.0479826534344	6.34683409239E-27	2.39841986132E+16	1E+15	2.50167521691E+16	120
0.0492194372194	2.12451662366E-25	2.60634467518E+16	1E+15	2.70669670674E+16	124
0.0504951208621	5.73929239594E-24	2.81194143968E+16	1E+15	2.91550921724E+16	128

## Fermi energy vs. temperature

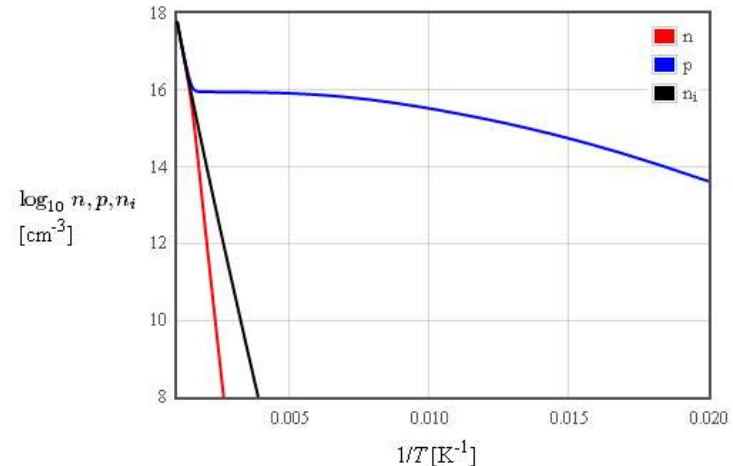
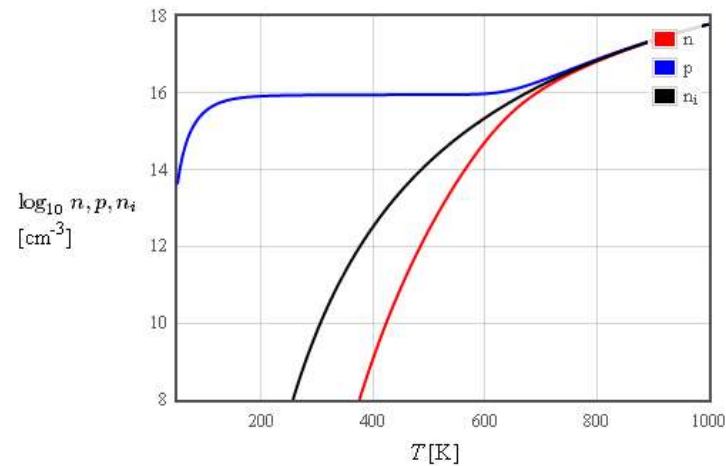
Fermi energy of an extrinsic semiconductor is plotted as a function of temperature. At each temperature the Fermi energy was calculated by requiring that charge neutrality be satisfied.



$N_c(300\text{ K}) = 2.78\text{E}19$	1/cm <sup>3</sup>	Semiconductor <input type="button" value="Si"/> <input type="button" value="Ge"/> <input type="button" value="GaAs"/>
$N_v(300\text{ K}) = 9.84\text{E}18$	1/cm <sup>3</sup>	
$E_g = 1.166 - 4.73\text{E-}4 * T * T / (T + 636)$	eV	
$N_d = 1\text{E}15$	1/cm <sup>3</sup>	Donor <input type="button" value="P in Si"/> <input type="button" value="P in Ge"/> <input type="button" value="Si in GaAs"/>
$E_c - E_d = 0.045$	eV	
$N_a = 1\text{E}16$	1/cm <sup>3</sup>	Acceptor <input type="button" value="B in Si"/> <input type="button" value="B in Ge"/> <input type="button" value="Si in GaAs"/>
$E_a - E_v = 0.045$	eV	
$T_1 = 50$	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  $n_i = \sqrt{N_c \left(\frac{T}{300}\right)^{3/2} N_v \left(\frac{T}{300}\right)^{3/2} \exp\left(\frac{-E_g}{2k_B T}\right)}$ .

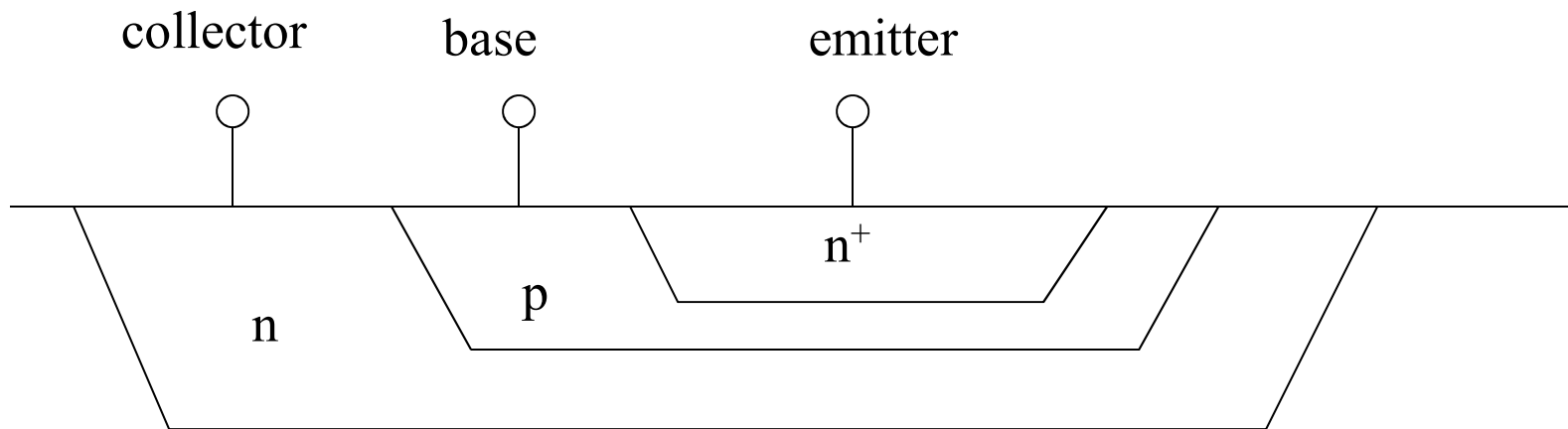


<http://lamp.tu-graz.ac.at/~hadley/psd/L4/eftplot.html>

# Why dope with donors AND acceptors?

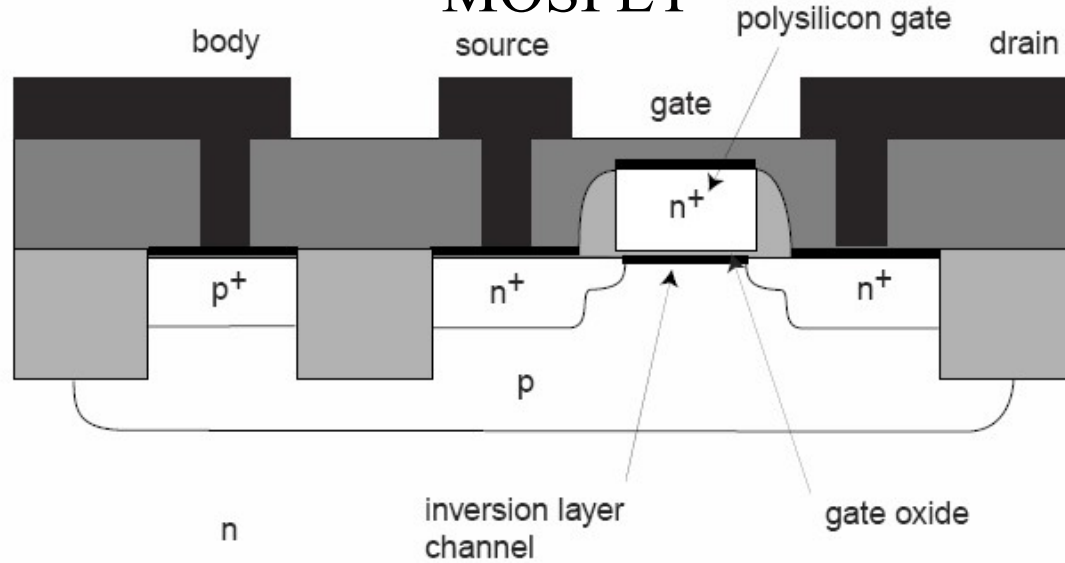
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Bipolar transistor

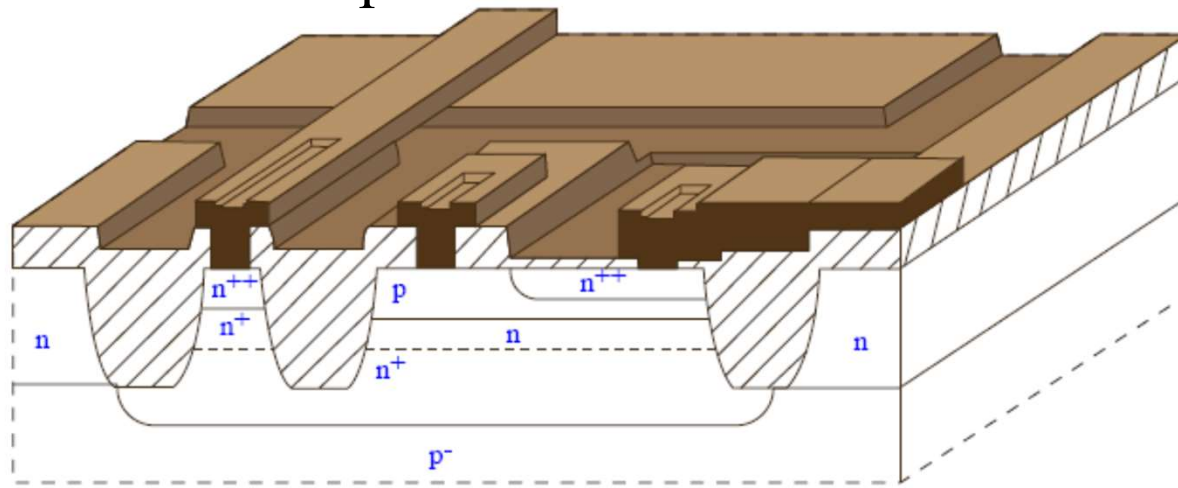


lightly doped p substrate

# MOSFET

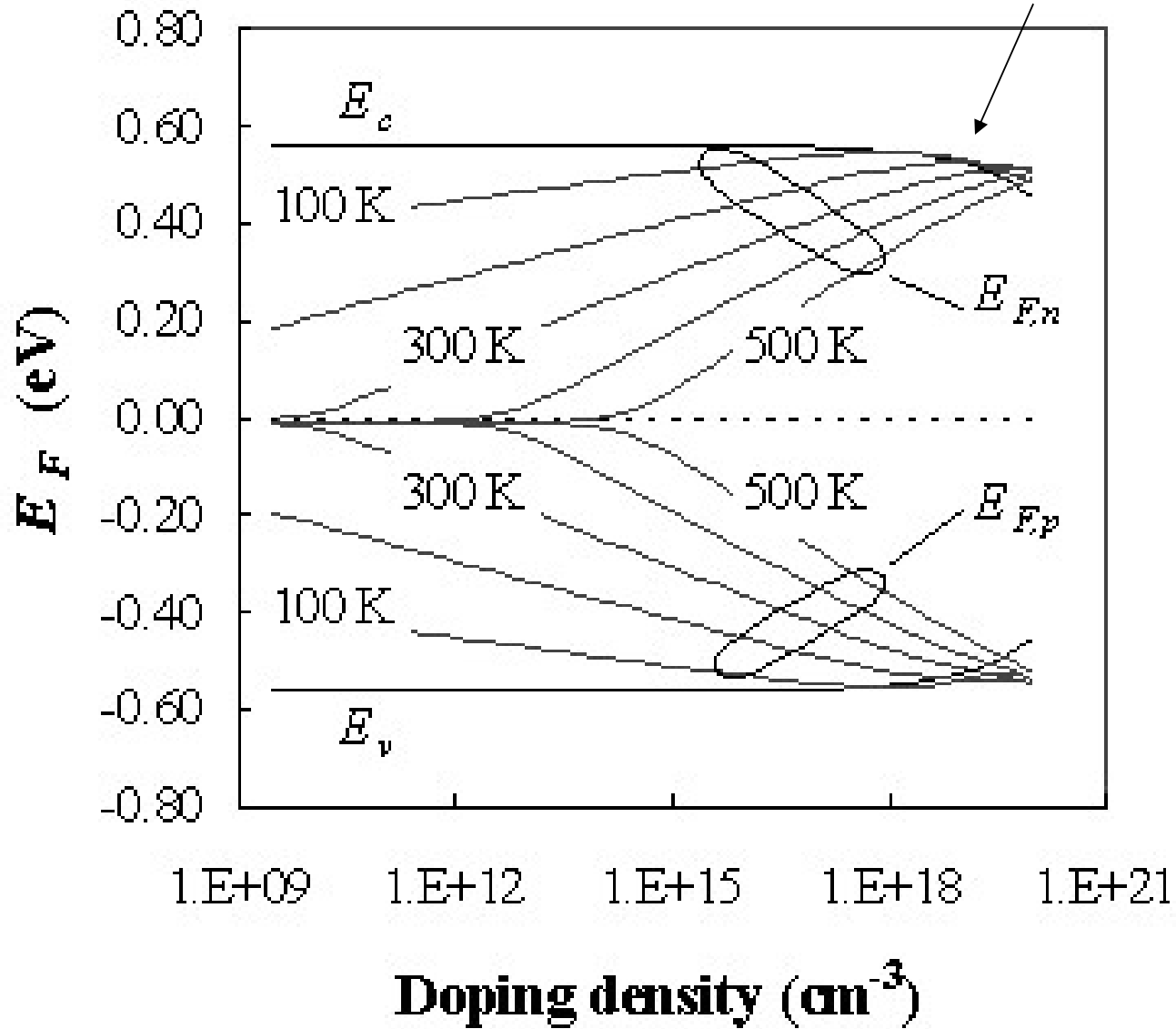


# Bipolar Junction Transistor



**Oxide isolated integrated BJT - a modern process**

degenerately doped semiconductor



# Degenerate semiconductor

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Heavily doped semiconductors are called degenerately doped

$N_D > 0.1 N_c \rightarrow E_F$  in the conduction band

$N_A > 0.1 N_v \rightarrow E_F$  in the valence band

Heavy doping narrows the band gap

The Boltzmann approximation is not valid

Degenerate semiconductors = metal

# Carrier transport

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# Carrier Transport

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Ballistic transport

Drift

Diffusion

Generation and recombination

The continuity equation

High field effects



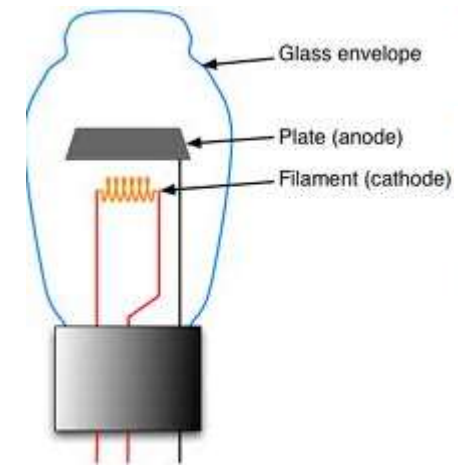
# Ballistic transport

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$$\vec{F} = m\vec{a} = -e\vec{E} = m \frac{d\vec{v}}{dt}$$

$$\vec{v} = \frac{-e\vec{E}t}{m} + \vec{v}_0$$

$$\vec{x} = \frac{-e\vec{E}t^2}{2m} + \vec{v}_0t + \vec{x}_0$$



Electrons moving in an electric field follow parabolic trajectories like a ball in a gravitational field.

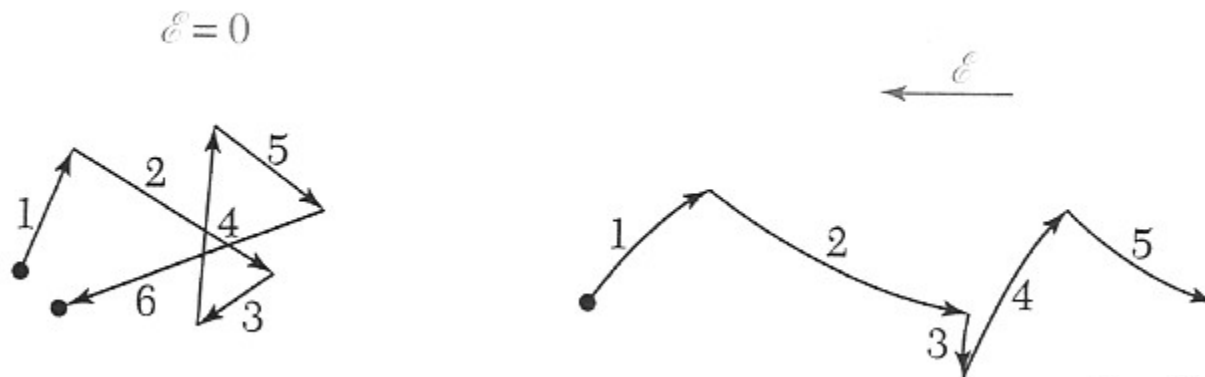
# Drift

The electrons scatter and change direction after a time  $\tau_{sc}$ .

Classical equipartition:  $\frac{1}{2} m v_{th}^2 = \frac{3}{2} k_B T$

At 300 K,  $v_{th} \sim 10^7$  cm/s.

mean free path:  $\ell = v_{th} \tau_{sc} \sim 10$  nm  $\sim 200$  atoms



# Drift (diffusive transport)

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$$\vec{F} = -e\vec{E} = m^* \vec{a} = m^* \frac{d\vec{v}}{dt}$$

$$\vec{v} = \vec{v}_0 - \frac{e\vec{E}}{m^*} (t - t_0)$$

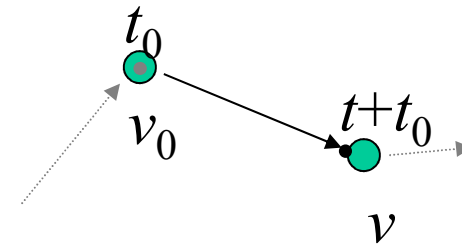
$$\langle \vec{v}_0 \rangle = 0 \quad \langle t - t_0 \rangle = \tau_{sc}$$

$$\vec{v}_d = \frac{-e\vec{E}\tau_{sc}}{m^*} = \frac{-e\vec{E}\ell}{m^* v}$$

drift velocity:  $\vec{v}_{d,n} = -\mu_n \vec{E}$

$$\vec{v}_{d,p} = \mu_p \vec{E}$$

*time between two collisions*



# Drift

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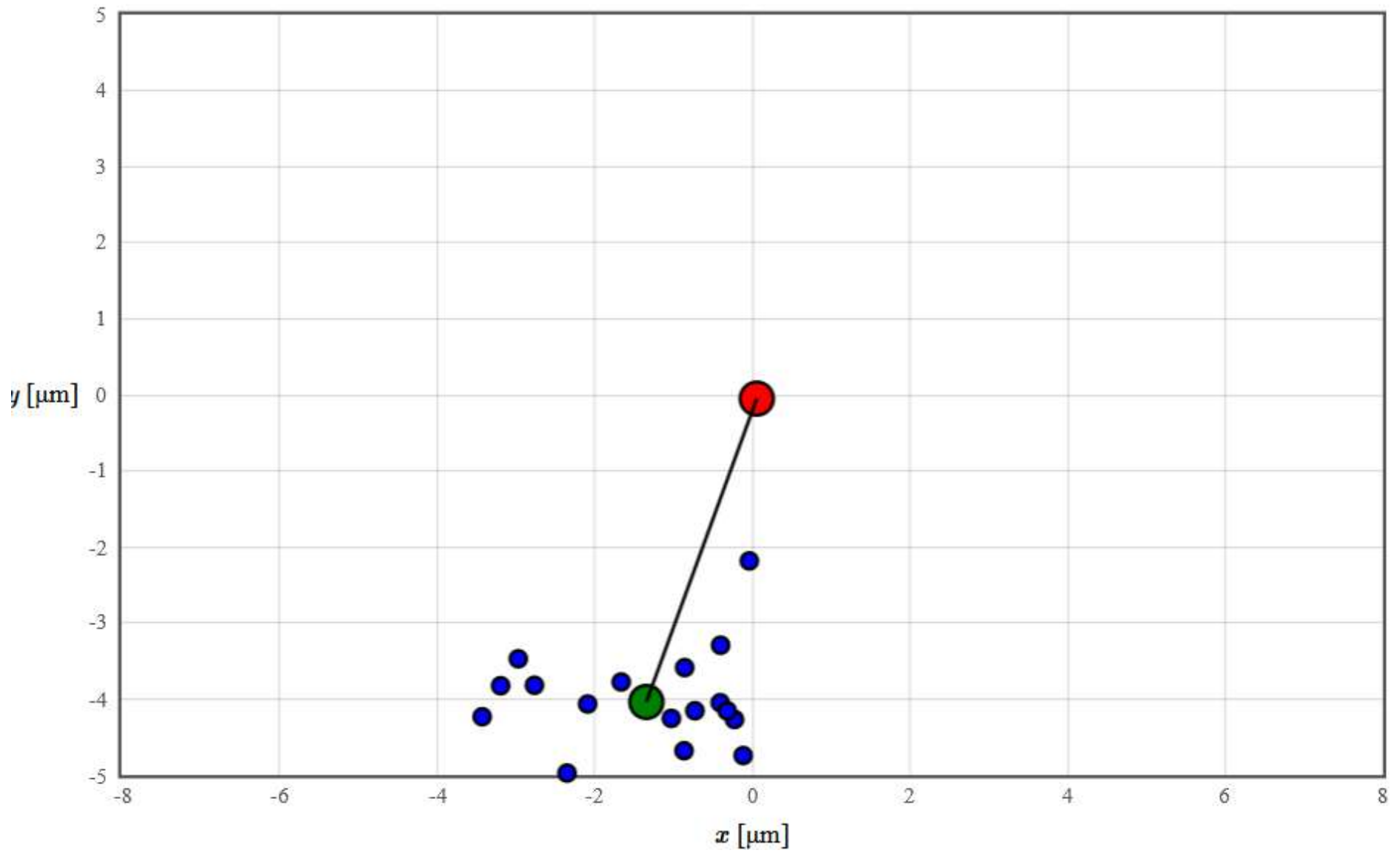
drift velocity:  $\vec{v}_{d,n} = -\mu_n \vec{E}$        $\vec{v}_{d,p} = \mu_p \vec{E}$

$$\vec{j} = -ne\vec{v}_{d,n} + pe\vec{v}_{d,p} = (ne\mu_n + pe\mu_p) \vec{E} = \sigma \vec{E}$$

$$\mu = \frac{-e\tau_{sc}}{m^*} = \frac{-e\ell}{m^* v}$$

for Si:  $\mu_n = 1350 \text{ cm}^2/\text{Vs}$   
 $\mu_p = 450 \text{ cm}^2/\text{Vs}$

For  $E = 1000 \text{ V/cm}$        $v_d = 10^6 \text{ cm/s}$



<http://lampx.tugraz.at/~hadley/psd/L5/drude.php>

# Drift

		$E_g$ (eV)	$\mu_n$ (cm <sup>2</sup> /V-s)	$\mu_p$ (cm <sup>2</sup> /V-s)	$m_n^*/m_0$ ( $m_l, m_t$ )	$m_p^*/m_0$ ( $m_{lh}, m_{hh}$ )	$a$ (Å)	$\epsilon_r$	Density (g/cm <sup>3</sup> )	Melting point (°C)
Si	(i/D)	1.11	1350	480	0.98, 0.19	0.16, 0.49	5.43	11.8	2.33	1415
Ge	(i/D)	0.67	3900	1900	1.64, 0.082	0.04, 0.28	5.65	16	5.32	936
SiC ( $\alpha$ )	(i/W)	2.86	500	—	0.6	1.0	3.08	10.2	3.21	2830
AlP	(i/Z)	2.45	80	—	—	0.2, 0.63	5.46	9.8	2.40	2000
AlAs	(i/Z)	2.16	1200	420	2.0	0.15, 0.76	5.66	10.9	3.60	1740
AlSb	(i/Z)	1.6	200	300	0.12	0.98	6.14	11	4.26	1080
GaP	(i/Z)	2.26	300	150	1.12, 0.22	0.14, 0.79	5.45	11.1	4.13	1467
GaAs	(d/Z)	1.43	8500	400	0.067	0.074, 0.50	5.65	13.2	5.31	1238
GaN	(d/Z, W)	3.4	380	—	0.19	0.60	4.5	12.2	6.1	2530
GaSb	(d/Z)	0.7	5000	1000	0.042	0.06, 0.23	6.09	15.7	5.61	712
InP	(d/Z)	1.35	4000	100	0.077	0.089, 0.85	5.87	12.4	4.79	1070
InAs	(d/Z)	0.36	22600	200	0.023	0.025, 0.41	6.06	14.6	5.67	943
InSb	(d/Z)	0.18	10 <sup>5</sup>	1700	0.014	0.015, 0.40	6.48	17.7	5.78	525
ZnS	(d/Z, W)	3.6	180	10	0.28	—	5.409	8.9	4.09	1650*
ZnSe	(d/Z)	2.7	600	28	0.14	0.60	5.671	9.2	5.65	1100*
ZnTe	(d/Z)	2.25	530	100	0.18	0.65	6.101	10.4	5.51	1238*
CdS	(d/W, Z)	2.42	250	15	0.21	0.80	4.137	8.9	4.82	1475
CdSe	(d/W)	1.73	800	—	0.13	0.45	4.30	10.2	5.81	1258
CdTe	(d/Z)	1.58	1050	100	0.10	0.37	6.482	10.2	6.20	1098
PbS	(i/H)	0.37	575	200	0.22	0.29	5.936	17.0	7.6	1119
PbSe	(i/H)	0.27	1500	1500	—	—	6.147	23.6	8.73	1081
PbTe	(i/H)	0.29	6000	4000	0.17	0.20	6.452	30	8.16	925

Solid state electronic devices, Streetman and Banerjee

$$\vec{v}_{d,n} = -\mu_n \vec{E}$$

$$\vec{v}_{d,p} = \mu_p \vec{E}$$

$$\vec{j} = -nev_{d,n} + pev_{d,p} = (ne\mu_n + pe\mu_p) \vec{E} = \sigma \vec{E}$$

# Matthiessen's rule

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$$\frac{1}{\tau_{sc}} = \frac{1}{\tau_{sc,lattice}} + \frac{1}{\tau_{sc,impurity}}$$

↑  
phonons, temperature dependent

↑ mostly temperature independent

$$\frac{1}{\mu} = \frac{1}{\mu_{lattice}} + \frac{1}{\mu_{impurity}}$$

$$\sigma = \frac{1}{\rho} = ne\mu_n + pe\mu_p$$

↑  
doping increases the conductivity  
by increasing the carrier density  
but decreases the mobility