5
Extrinsic Semiconductors

October 29th, 2026

doping: small admixture of impurities

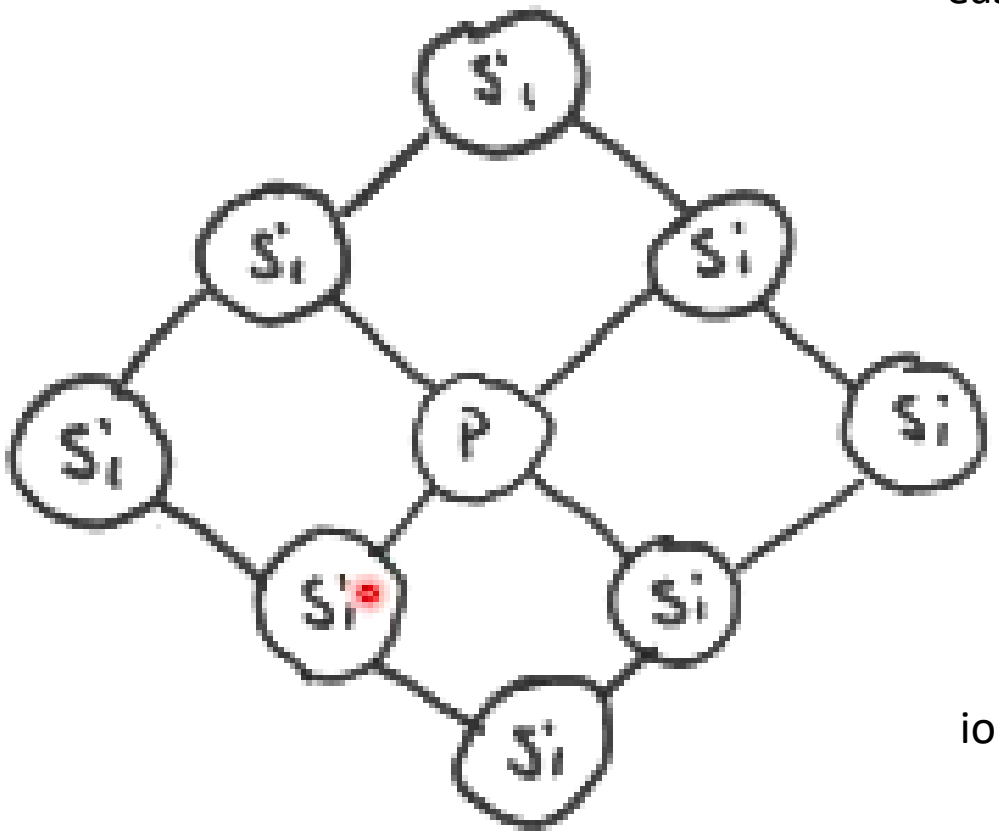
doping: impurity atoms that can add electrons or holes

n-doping: donor atoms add electrons in the conduction band **P, As in Si**

p-doping: acceptor atoms add holes in the valence band **Al, B, Ga in Si**

- change in macroscopic properties (electric conductivity)

Ionization of dopants



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

remove electron from ground state of a hydrogen-like impurity

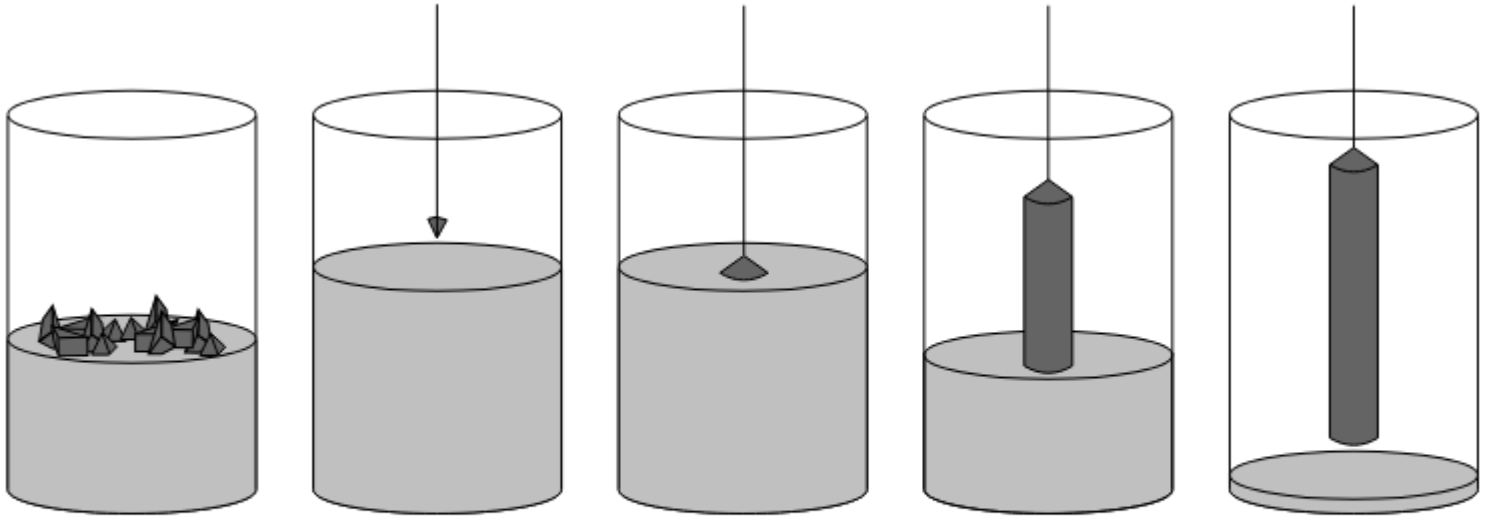
$$E_n = -\frac{me^4}{8\varepsilon_0^2 h^2 n^2}$$ ionization in H-atom

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

ionization energy ~25 meV

include dopants

Czochralski process



add dopants to the melt



image from wikipedia

include dopants

float zone process

neutron transmutation

$$^{30}Si + n \rightarrow {}^{31}Si + \gamma$$
$$^{31}Si \rightarrow {}^{31}P + e^{-} + \bar{\nu}_e$$

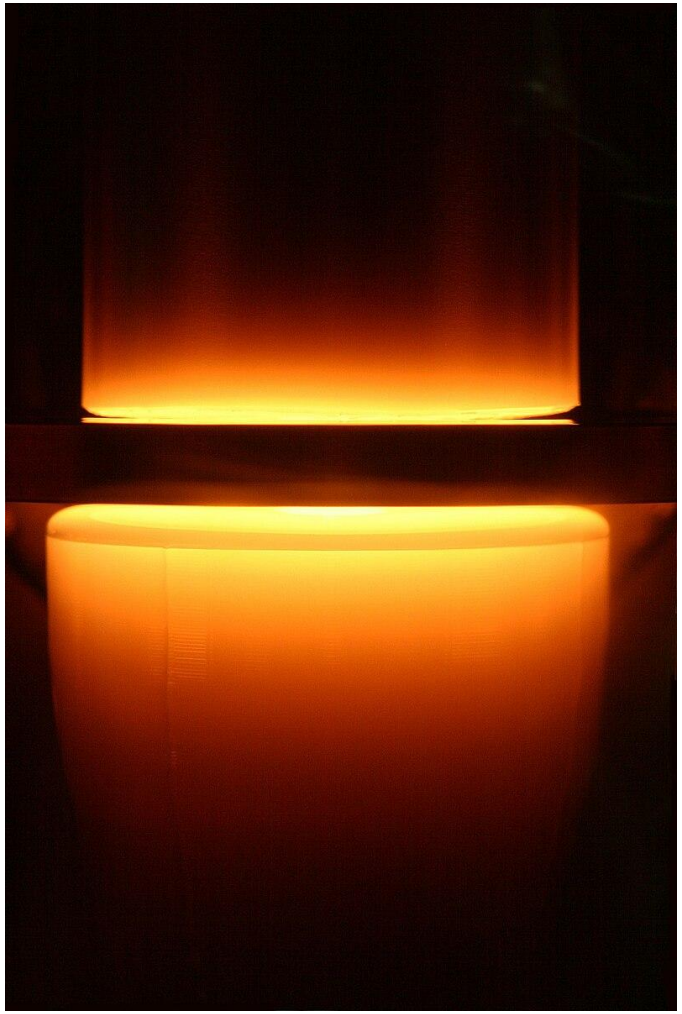


image from wikipedia

include dopants

gas phase diffusion

AsH_3 (arsine) or PH_3 (phosphine) for n-doping

B_2H_6 (diborane) for p-doping

chemical vapor deposition

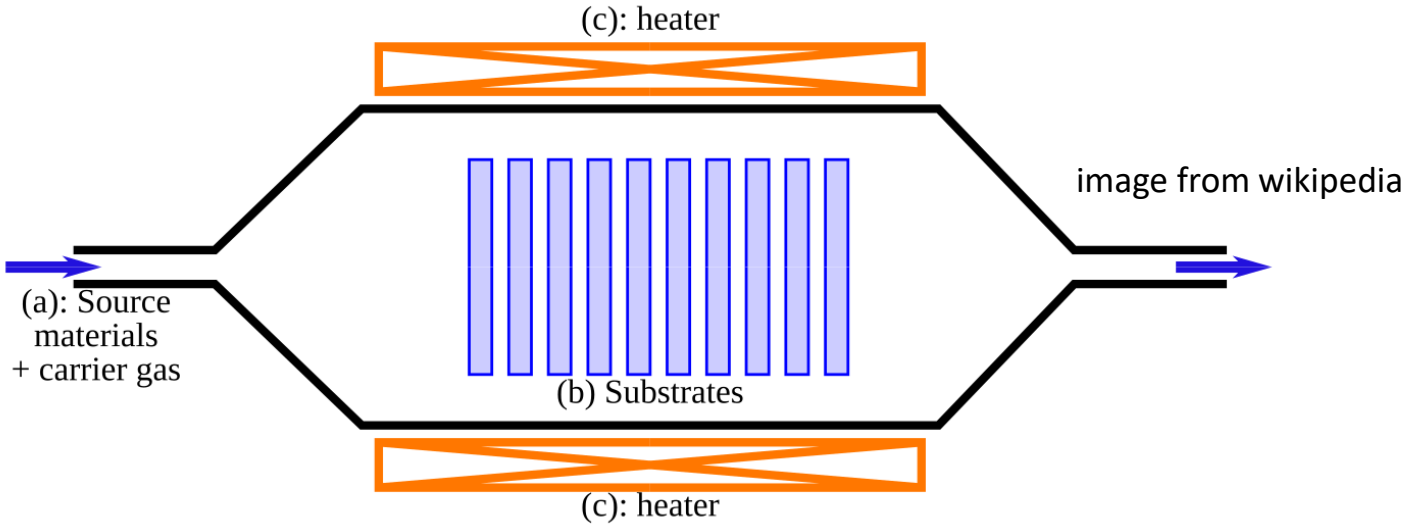


image from wikipedia

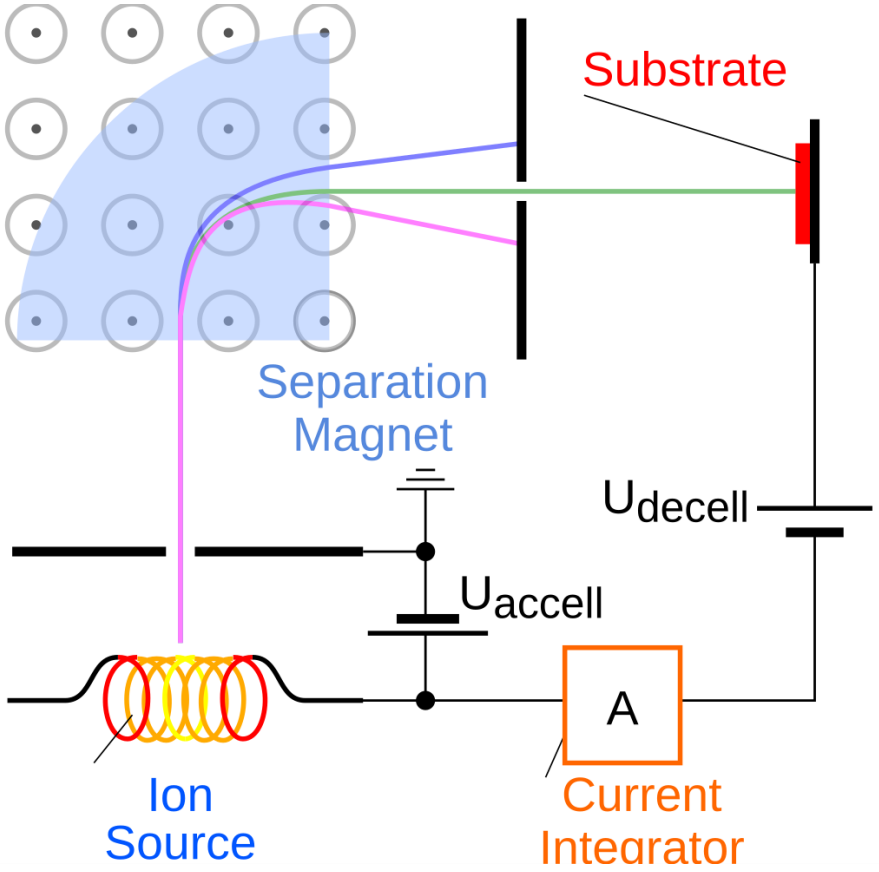
epitaxial silicon CVD SiH_4 (silane) or SiH_2Cl_2 (dichlorosilane)
PH_3 (phosphine) for n-doping or B_2H_6 (diborane) for p-doping

include dopants

ion implantation



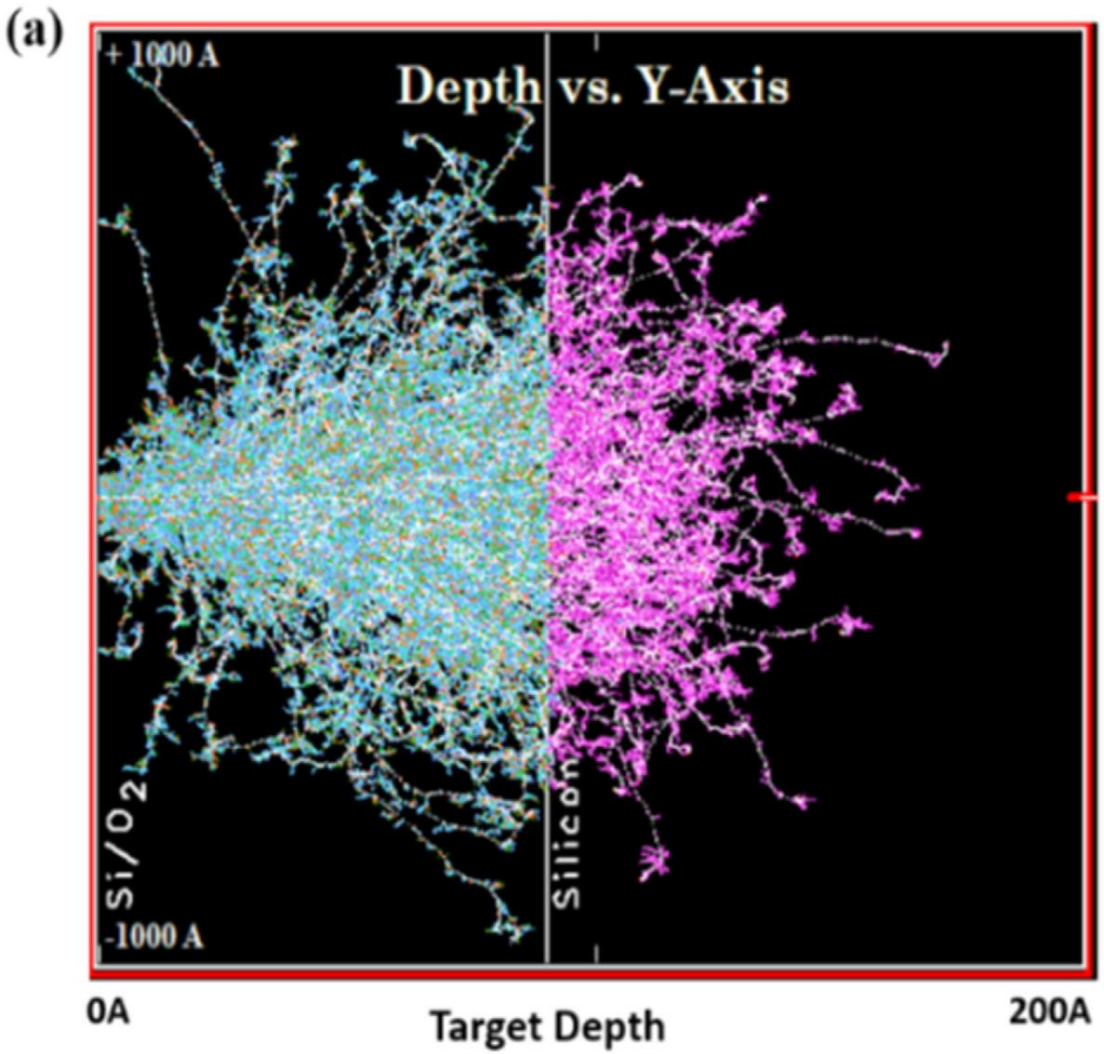
images from wikipedia

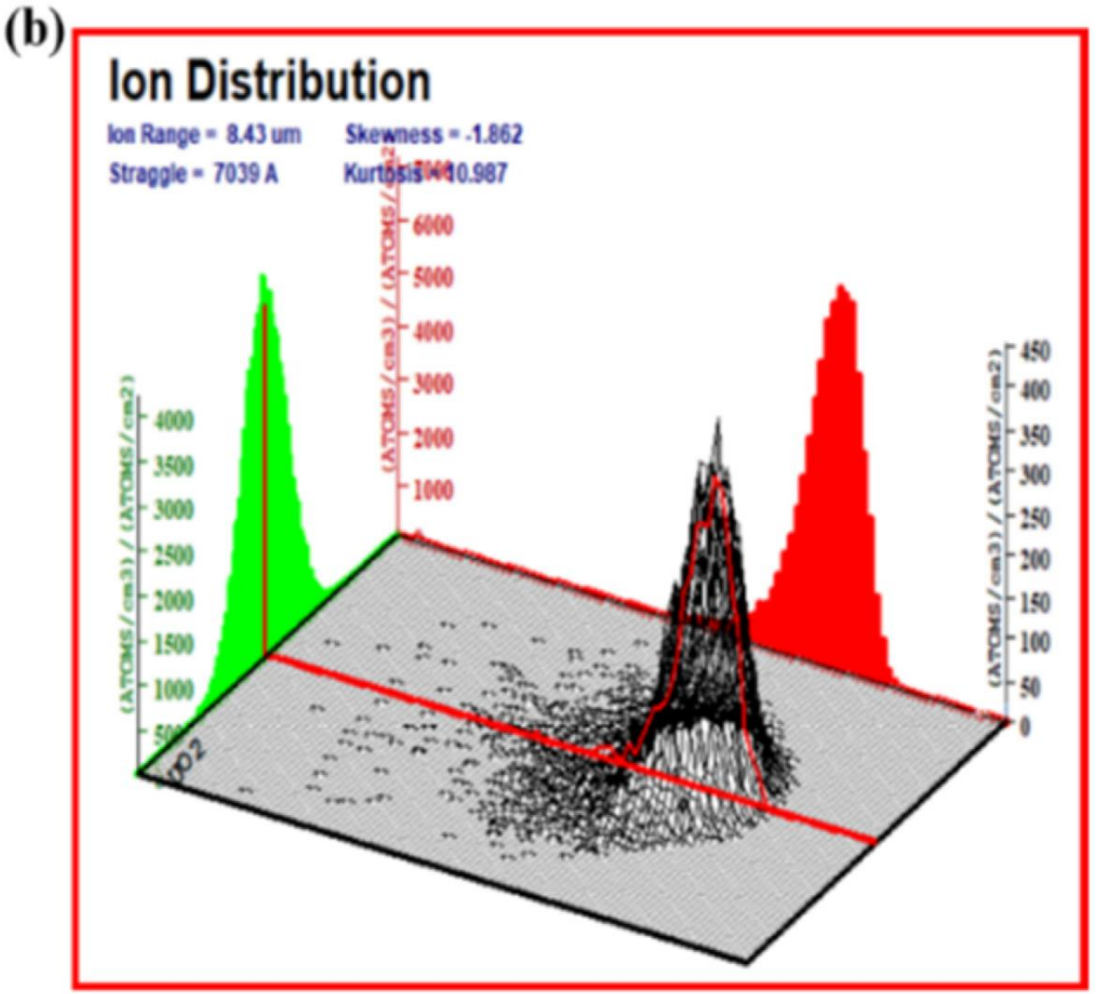


implant at 7 degrees to avoid channeling

Simulate dopant distribution

the stopping and range of ions in matter

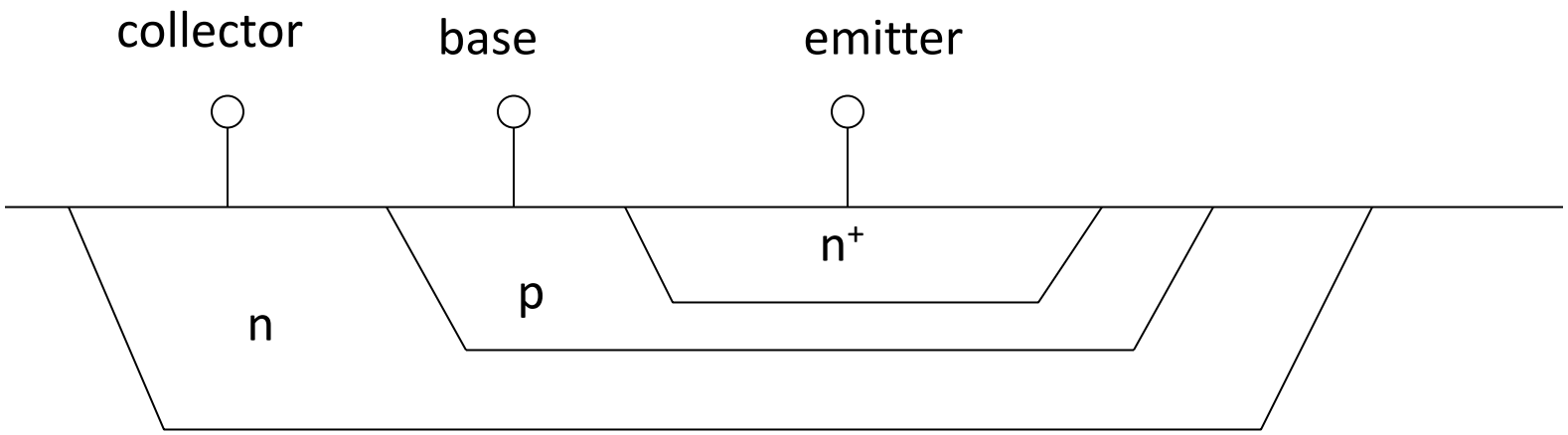




https://ars.els-cdn.com/content/image/1-s2.0-S173857332500138X-gr12_lrg.jpg

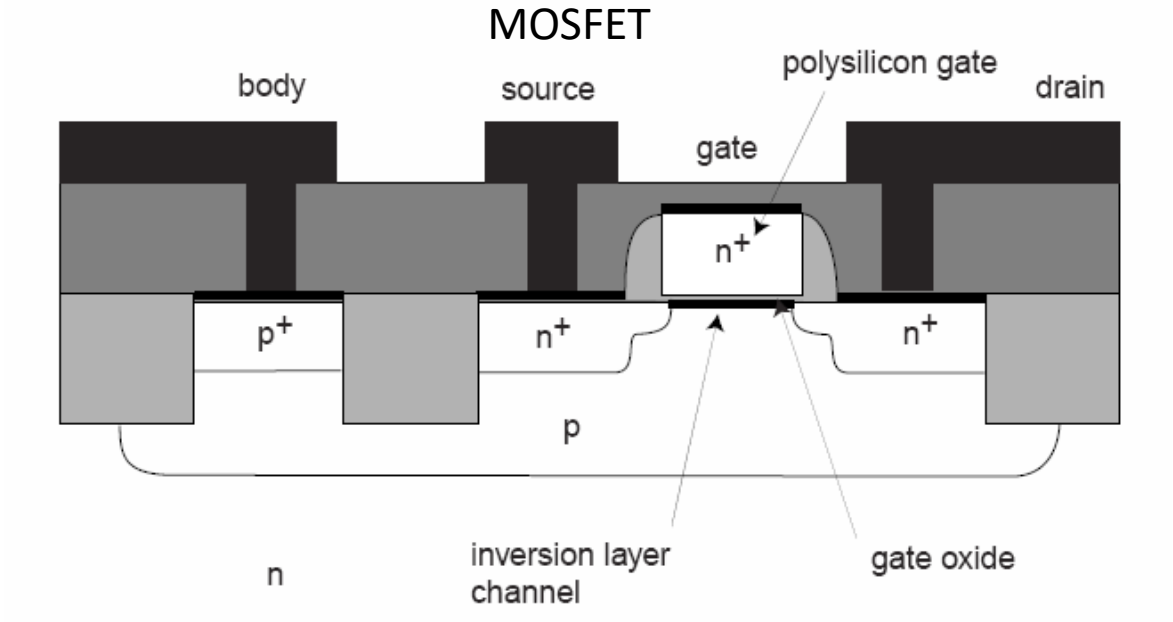
Why dope with donor and acceptors ?

Bipolar transistor

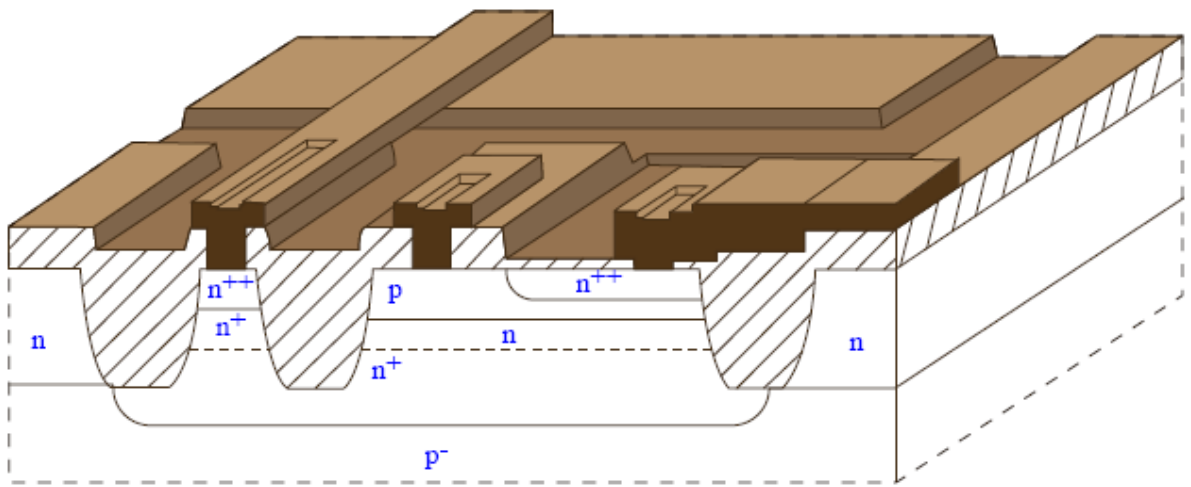


lightly doped p substrate

MOSFET



Bipolar Junction Transistor



Oxide isolated integrated BJT - a modern process

n and p?

$$n = N_c(T) \exp\left(\frac{E_F - E_c}{k_B T}\right)$$ are in the conduction band

$$p = N_v(T) \exp\left(\frac{E_v - E_F}{k_B T}\right)$$ are in the valence band

law of mass action

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

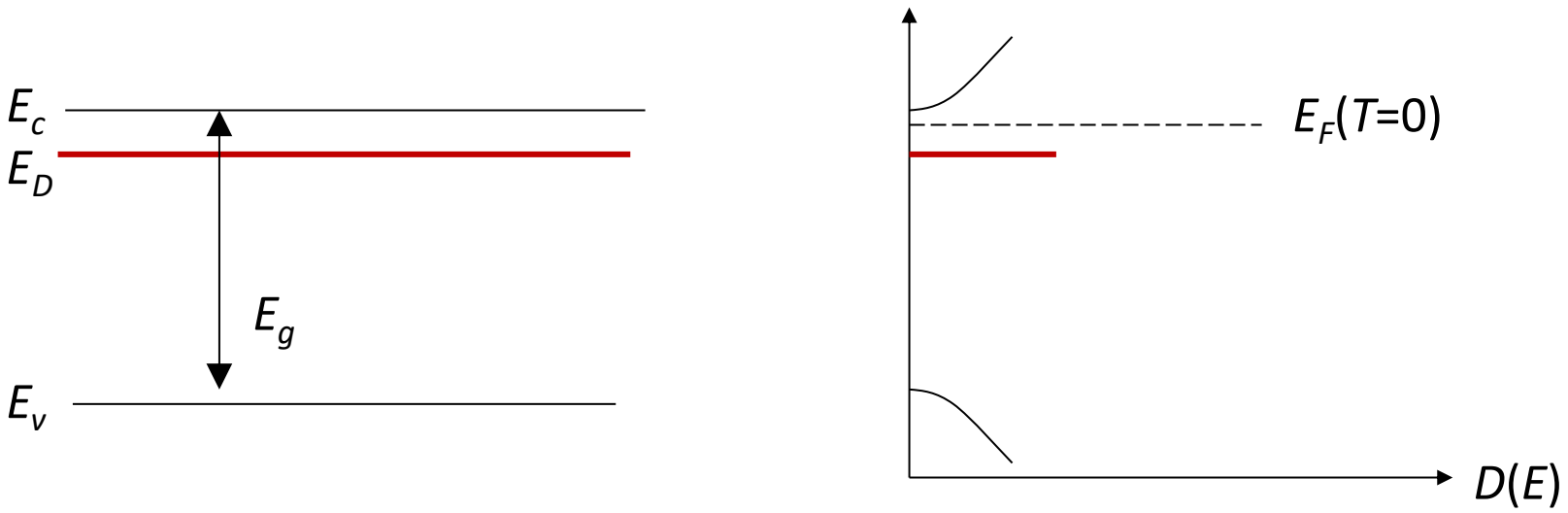
$$n_i = \sqrt{N_c N_v} \exp\left(\frac{E_g}{2k_B T}\right)$$

$$np = n_i^2$$

n-doping: increase number of electrons

Five valence electrons: P, As

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

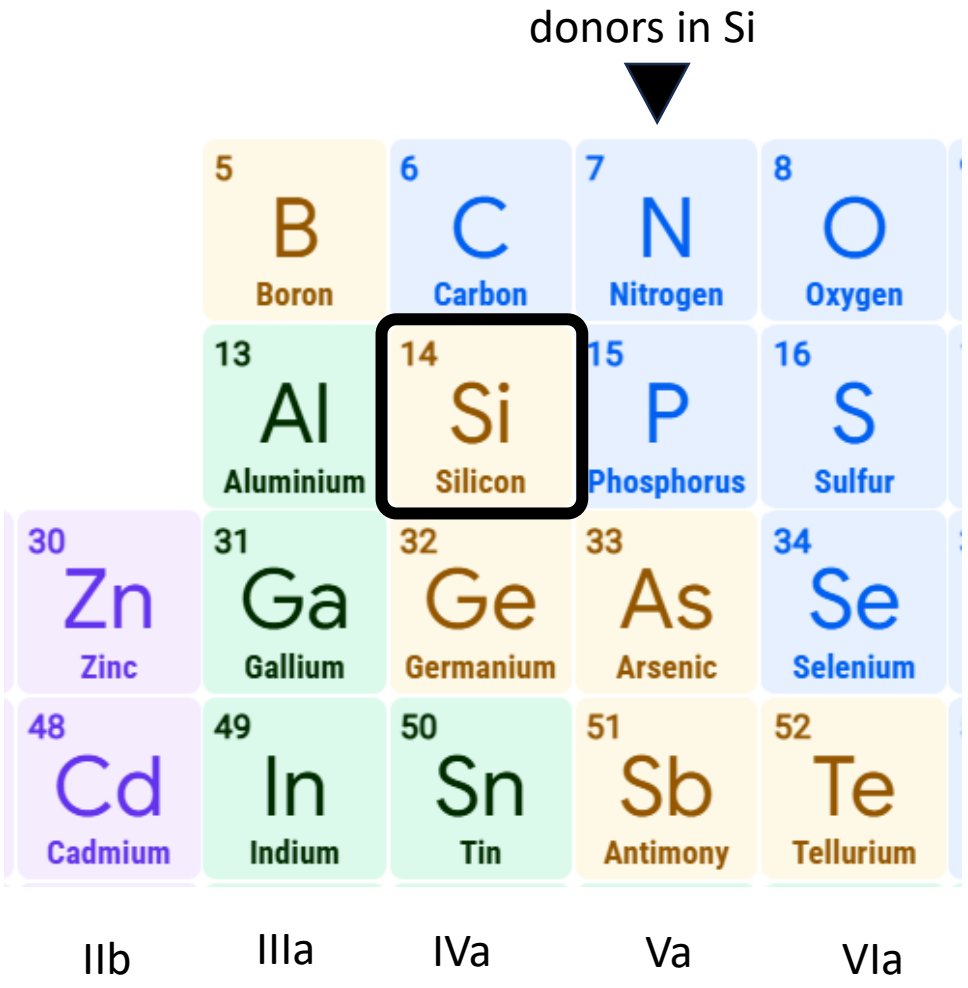


n-type: $n \sim N_D$

many more electrons in the conduction band than holes in the valence band.

majority carriers: electrons; minority carriers: holes

Donors for Si

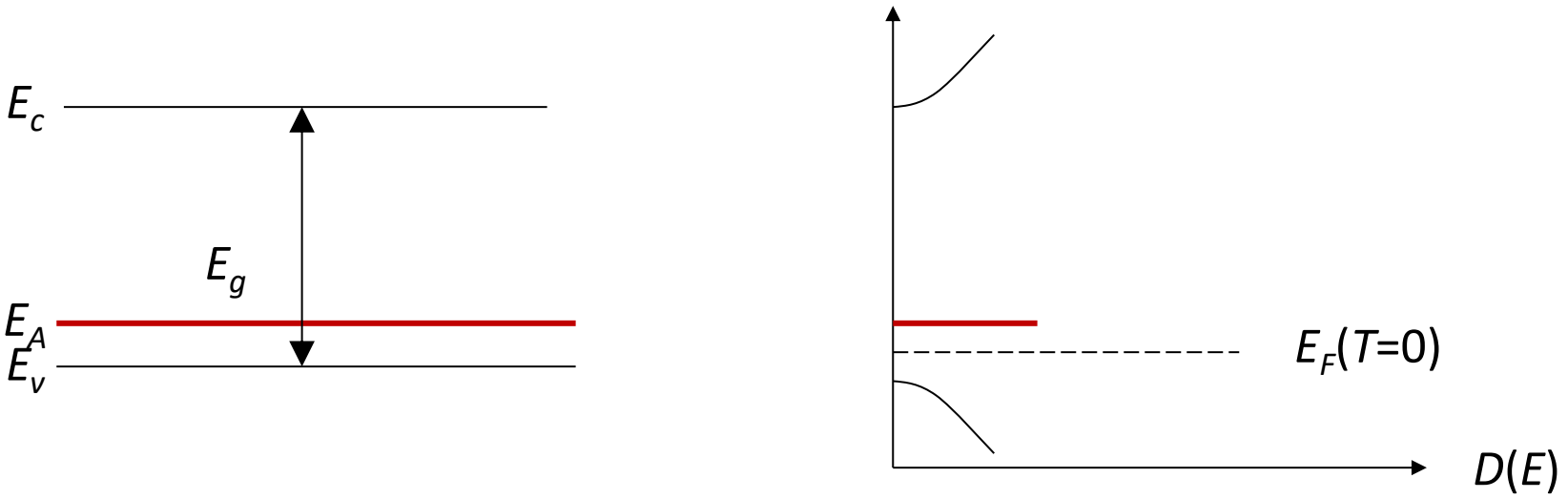


https://artsexperiments.withgoogle.com/periodic-table/?exp=true&lang=en

p-doping: increase number of holes

Three valence electrons: B, Al, Ga

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

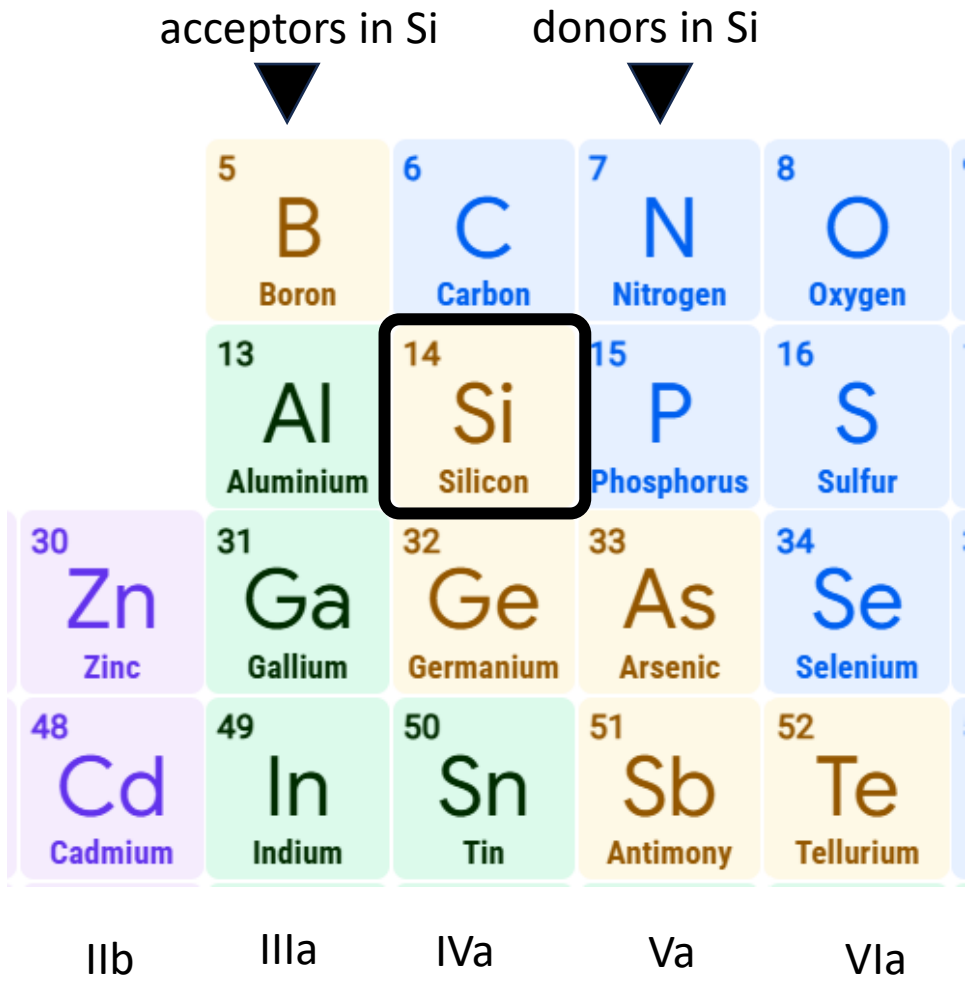


p-type: $p \sim N_A$
many more holes in the valence band than electrons in the conduction band

majority carriers: holes; minority carriers: electrons

Donors and Acceptors for Si

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https://artsexperiments.withgoogle.com/periodic-table/?exp=true&lang=en

Donor and Acceptor Energies

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

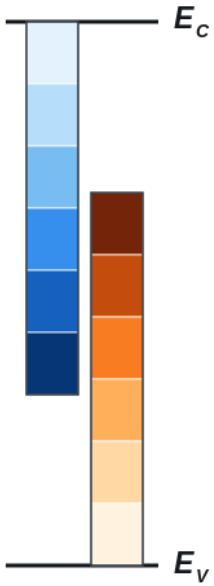
Donor and Acceptor Energies (in meV)

H						
Li 33	Be	**B 45**	C	N	O	F
Na	Mg	**Al 67**	**Si**	**P 45**	S	Cl
K	Ca	**Ga 72**	Ge	**As 54**	Se	Br
Rb	Sr	**In 160**	Sn	**Sb 39**	Te	I
Cs	Ba					

H						
Li 9.3	Be	**B 10**	C	N	O	F
Na	Mg	**Al 10**	Si	**P 12**	S	Cl
K	Ca	**Ga 11**	**Ge**	**As 13**	Se	Br
Rb	Sr	**In 11**	Sn	**Sb 9.6**	Te	I
Cs	Ba					

H						
Li	**Be 28**	B	**C 26**	N	O	F
Na	**Mg 28**	Al	**35 / 5.8**	P	**S 6**	Cl
K	Ca	**Ga**	**Ge 6**	**As**	Se	Br
Rb	Sr	In	**Sn 6**	Sb	Te	I
Cs	Ba					

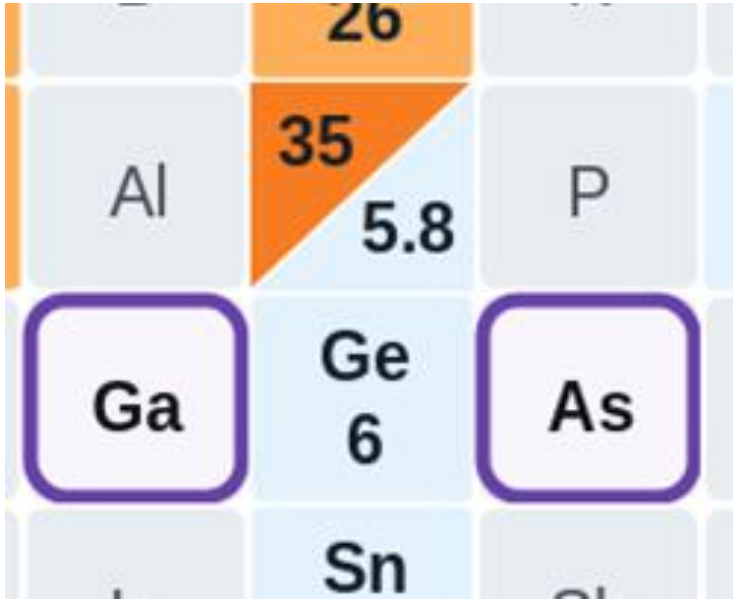
energy below the conduction band



energy above the valence band

Si as Donor and Acceptor for GaAs

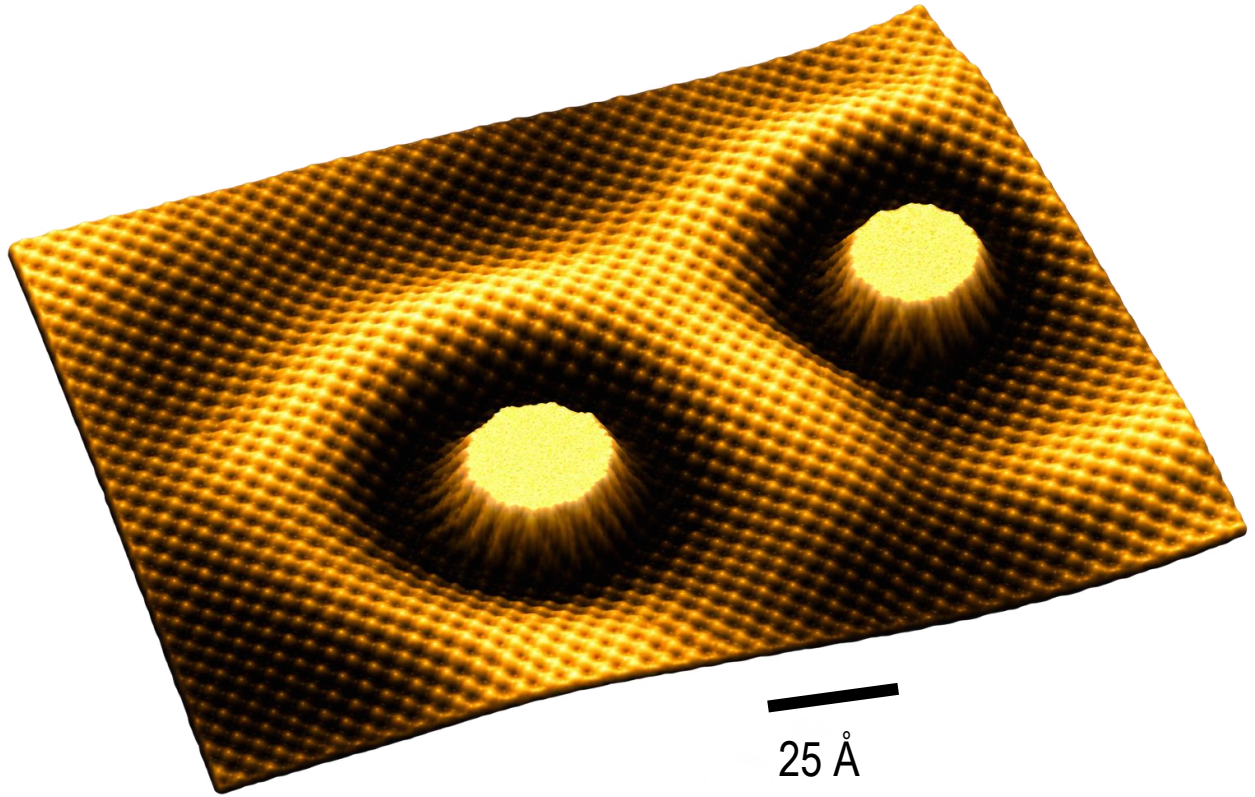
Si : donor or acceptor



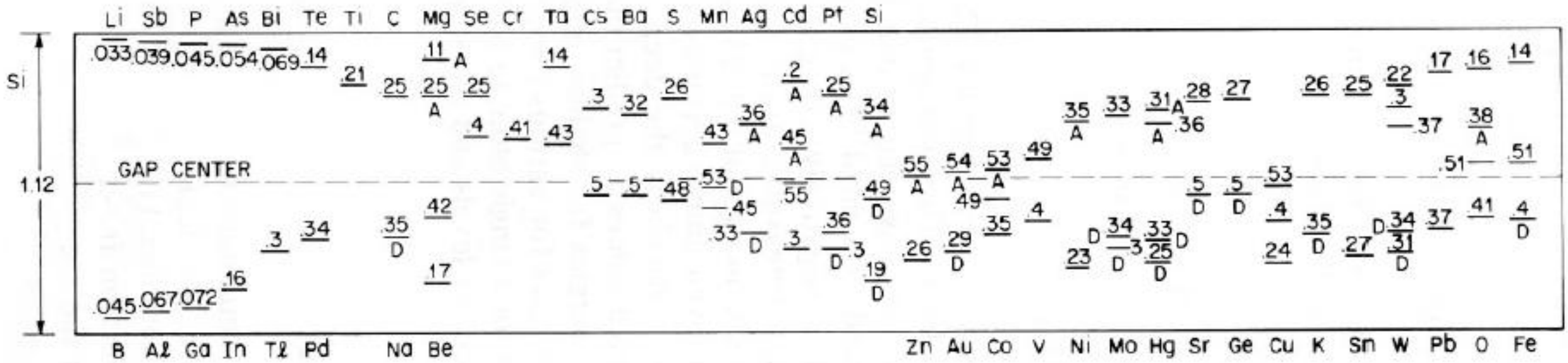
binding energy depends on Ga or As substitution

Direct Observation of Friedel Oscillations around Incorporated Si_{Ga} Dopants in GaAs by Low-Temperature Scanning Tunneling Microscopy

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(Received 25 July 1995)



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

Extrinsic semiconductors

Dopants

Donors

Examples: P, As in Si.

Mobile negative electrons

Fixed positive donors

Acceptors

Examples: B, Ga in Si.

Mobile positive holes

Fixed negative acceptors

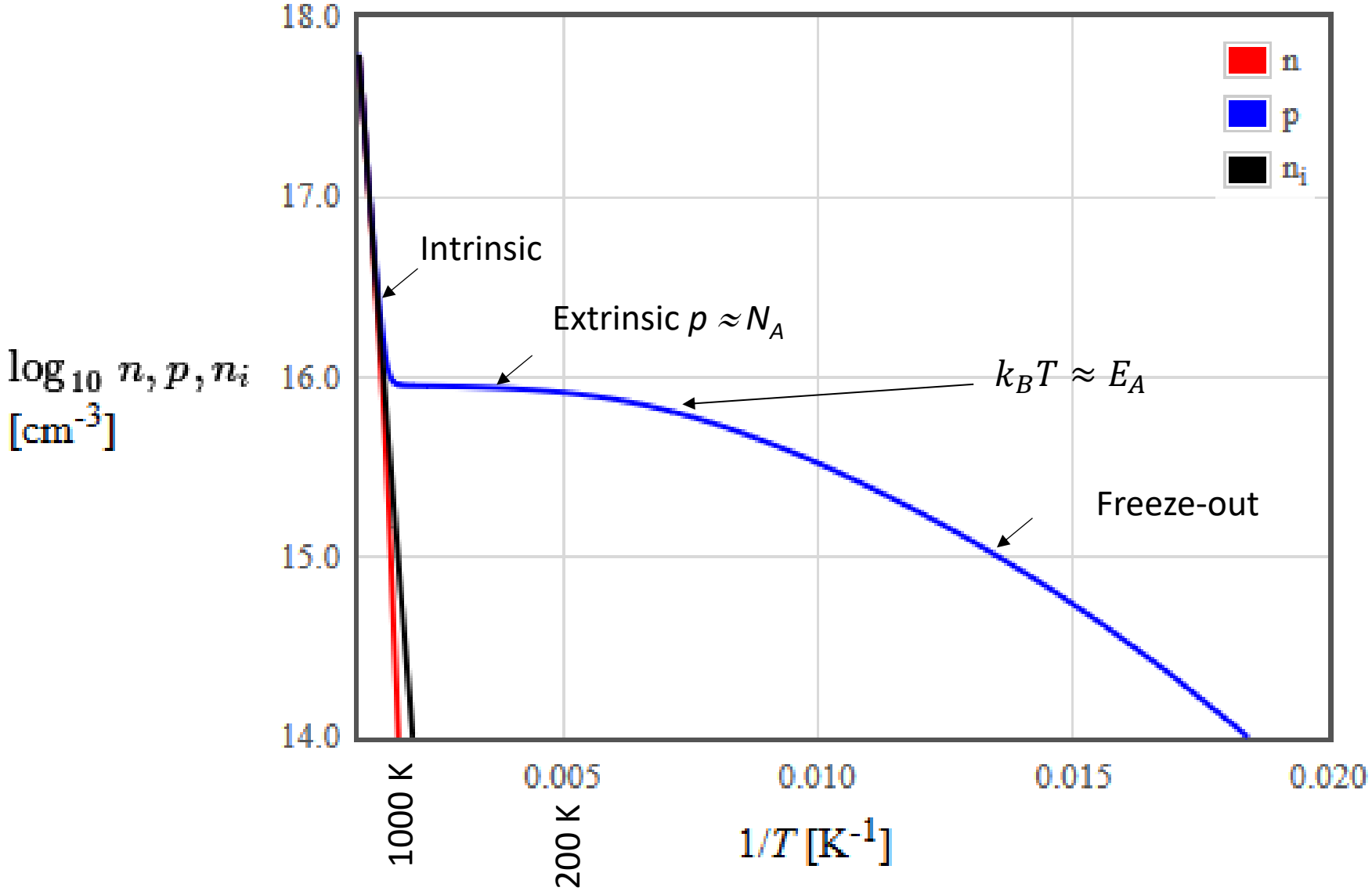
Charge Neutrality

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

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

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

Temperature dependence



Ionized donors and acceptors

For $E_v + 3k_BT < E_F < E_c - 3k_BT$ Boltzmann approximation

$$N_D^+ = \frac{N_D}{1 + 2\exp\left(\frac{E_F - E_D}{k_BT}\right)}$$

$$N_A^- = \frac{N_A}{1 + 4\exp\left(\frac{E_A - E_F}{k_BT}\right)}$$

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

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

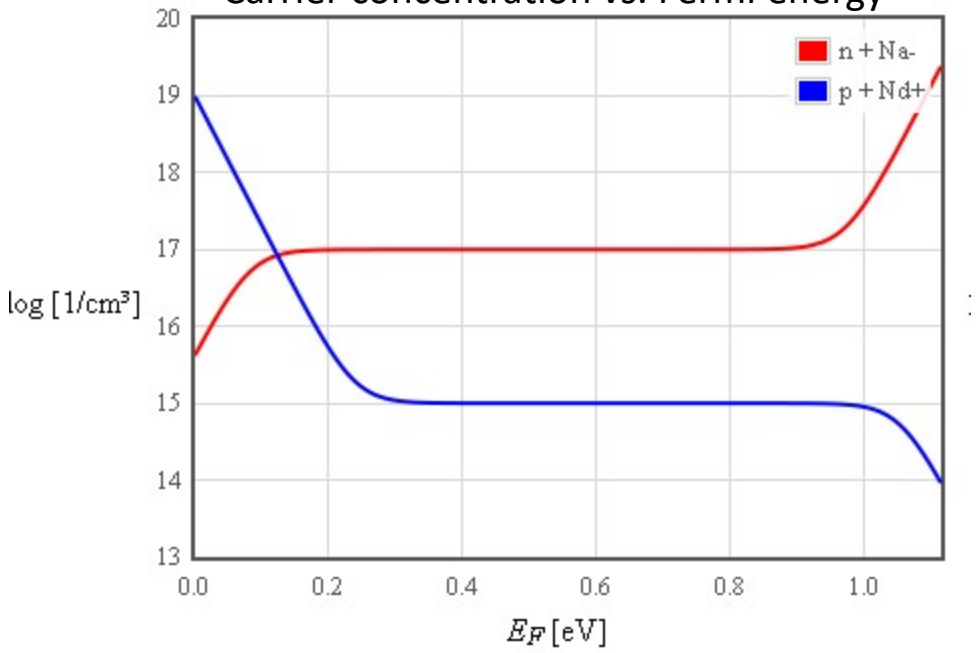
N_A = acceptor density cm^{-3} N_A^- = ionized acceptor density cm^{-3}

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

Ionized donors and acceptors

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

Carrier concentration vs. Fermi energy

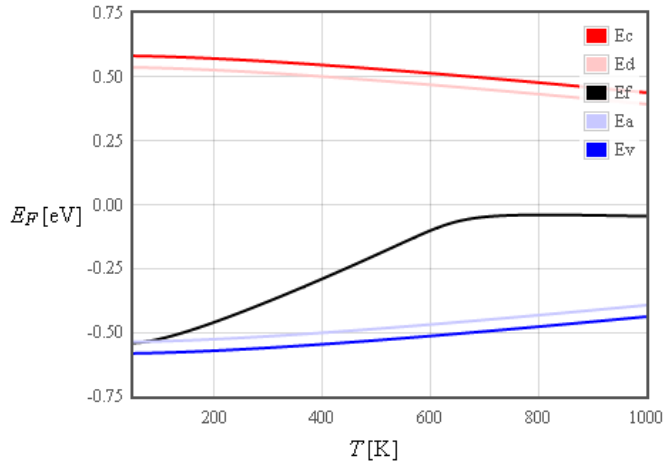



```
for ($i=0; $i<500; $i++) {
  $Ef = $i*$Eg/500;
  $n=$Nc*pow($T/300,1.5)*exp(1.6022E-19*($Ef-$Eg)/(1.38E-23*$T));
  $p=$Nv*pow($T/300,1.5)*exp(1.6022E-19*(-$Ef)/(1.38E-23*$T));
  $Namin = $Na/(1+4*exp(1.6022E-19*($Ea-$Ef)/(1.38E-23*$T)));
  $Ndplus = $Nd/(1+2*exp(1.6022E-19*($Ef-$Ed)/(1.38E-23*$T)));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

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	5.89310462781	6.95665036215E+18	1E+15	5.8356209035E+15	15.7660876057	18.8424631625

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 K) =	2.78E19	1/cm³
N_v(300 K) =	9.84E18	1/cm³
E_g =	1.166-4.73E-4*T*T/(T+636)	eV
N_d =	1E15	1/cm³
E_c - E_d =	0.045	eV
N_a =	1E16	1/cm³
E_a - E_v =	0.045	eV
T_1 =	50	K
T_2 =	1000	K

Replot

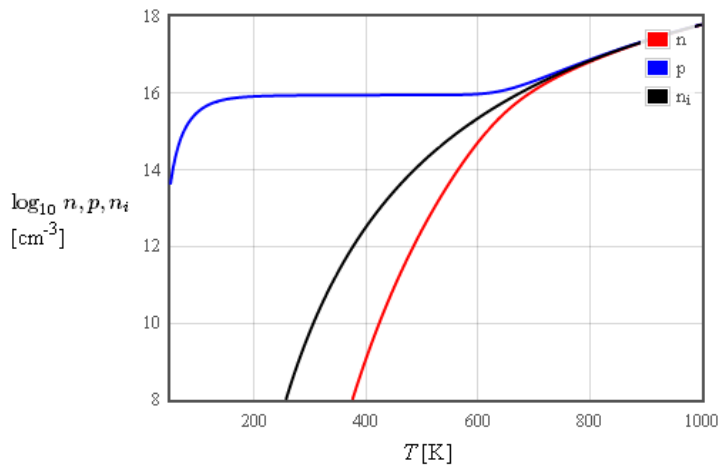
Semiconductor: Si | Ge | GaAs

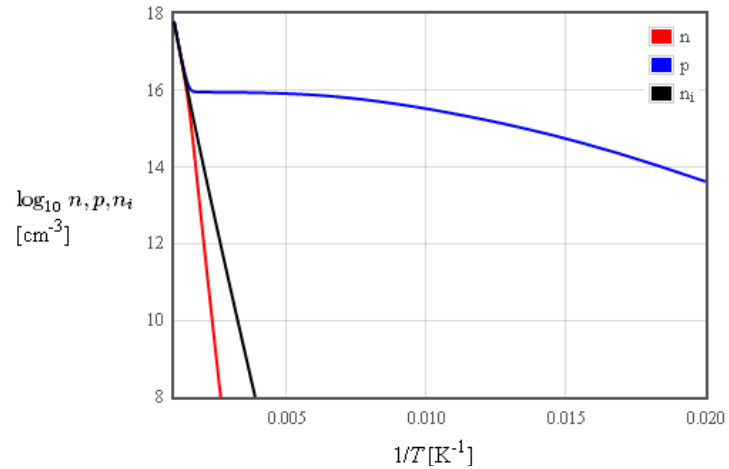
Donor: P in Si | P in Ge | Si in GaAs

Acceptor: B in Si | B in Ge | Si in GaAs

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 $p = N_v\left(\frac{T}{300}\right)^{3/2} \exp\left(\frac{E_v - E_F}{k_B T}\right)$.

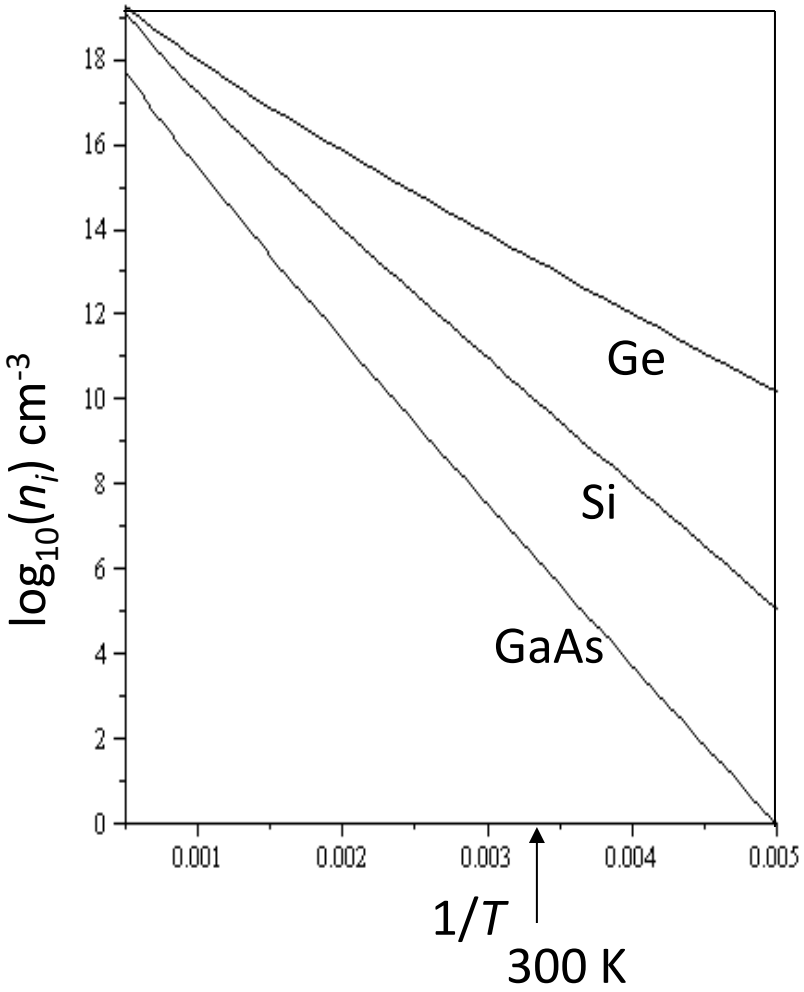
The intrinsic carrier density is $n_i = \sqrt{N_c\left(\frac{T}{300}\right)^{3/2} N_v\left(\frac{T}{300}\right)^{3/2}} \exp\left(\frac{-E_g}{2k_B T}\right)$.





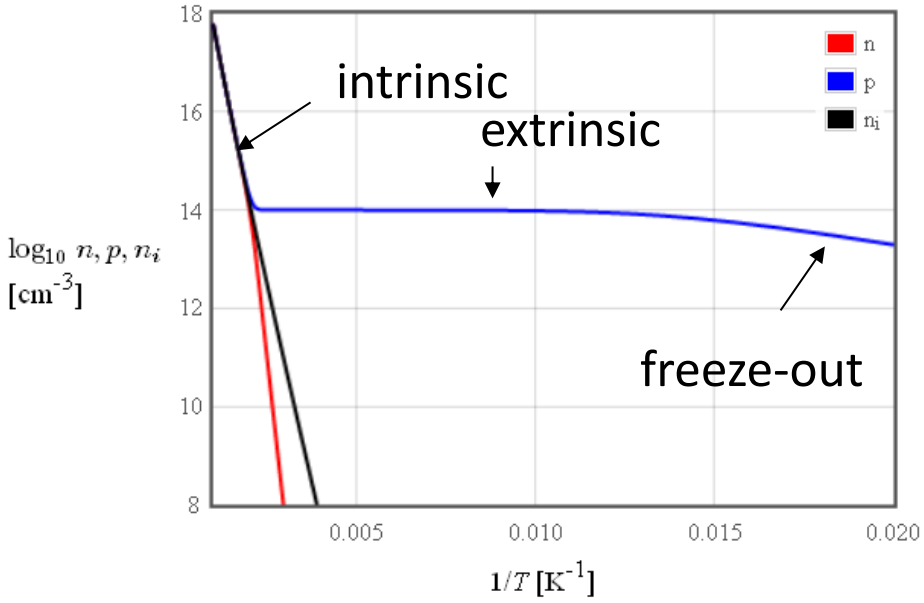
https://lampz.tugraz.at/~hadley/psd/L4/eftplot.html

Intrinsic semiconductors



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

Extrinsic semiconductors



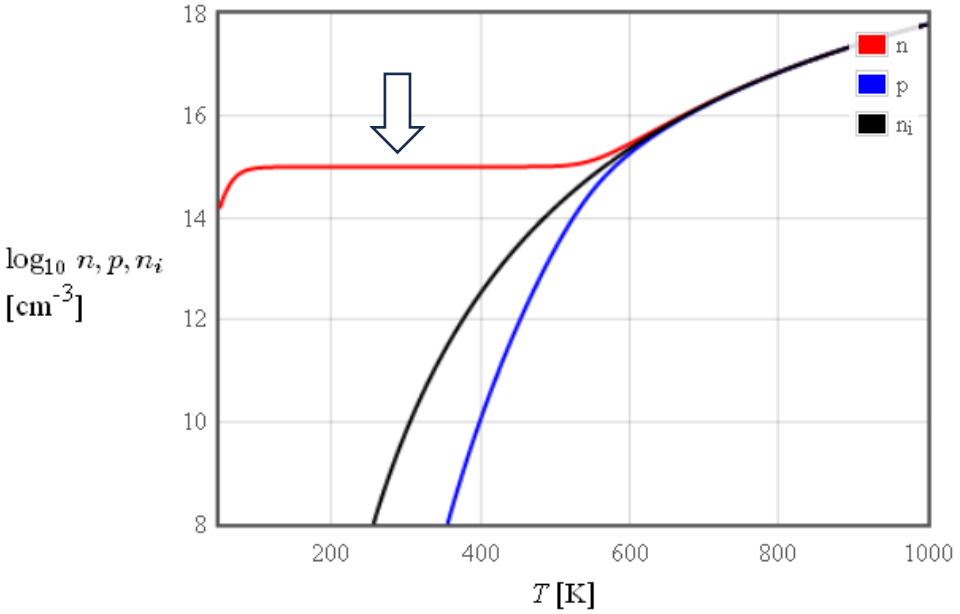
At high temperatures, extrinsic semiconductors have the same temperature dependence as intrinsic semiconductors.

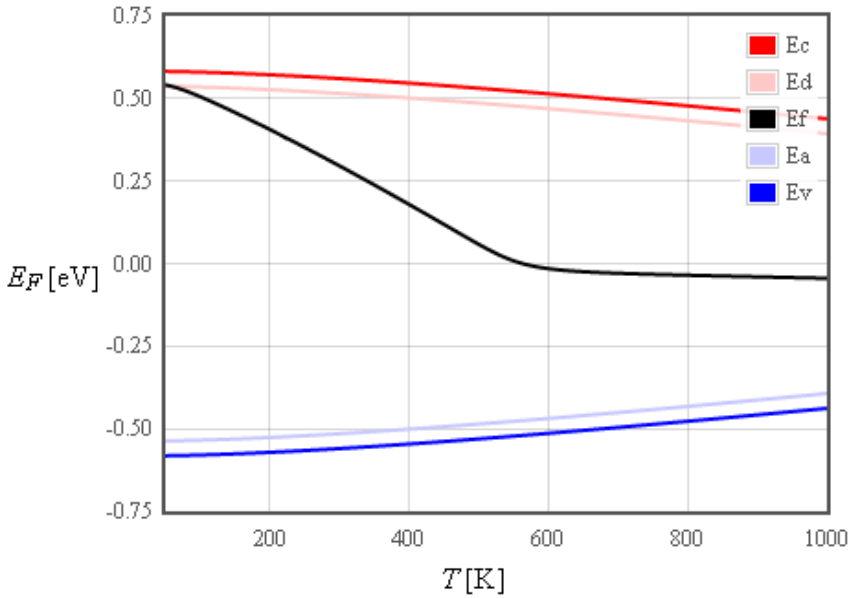
n-type (extrinsic)

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

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

For n-type:
n ~ density of donors,
$p = n_i^2 / N_D$



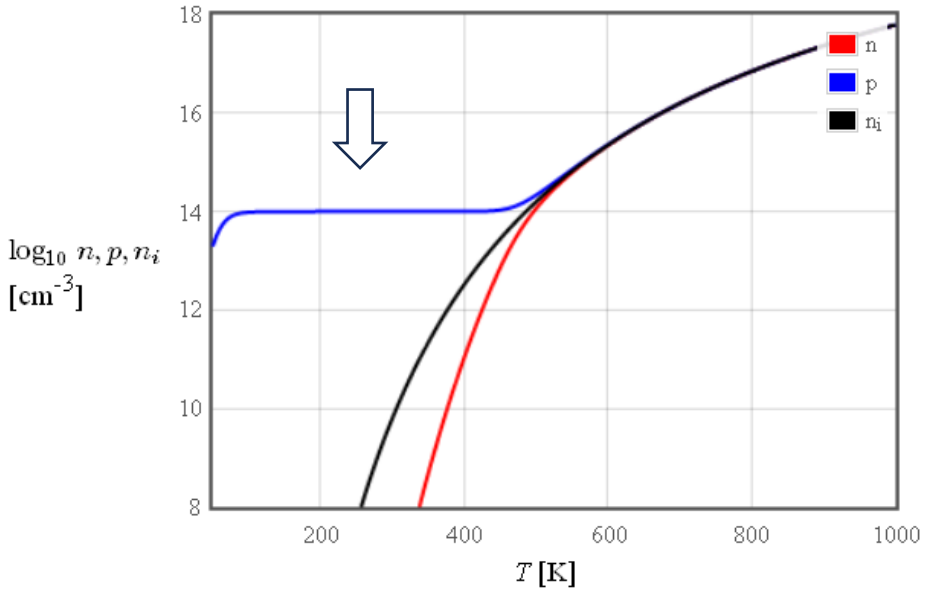


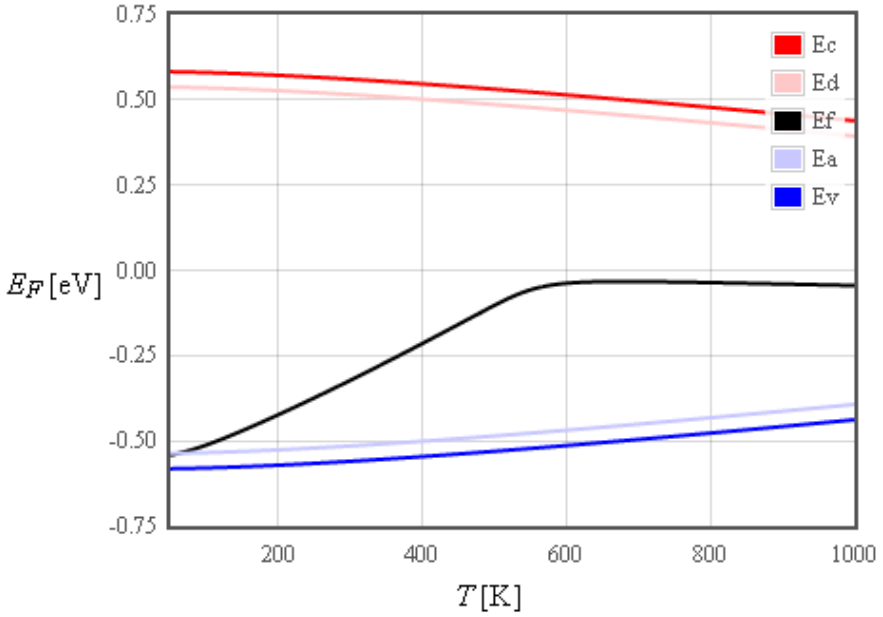
p-type (extrinsic)

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

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

For p-type,
p ~ density of acceptors,
$n = n_i^2/N_A$





Intrinsic / Extrinsic

Intrinsic: $n = p$

Conductivity **strongly temperature dependent**

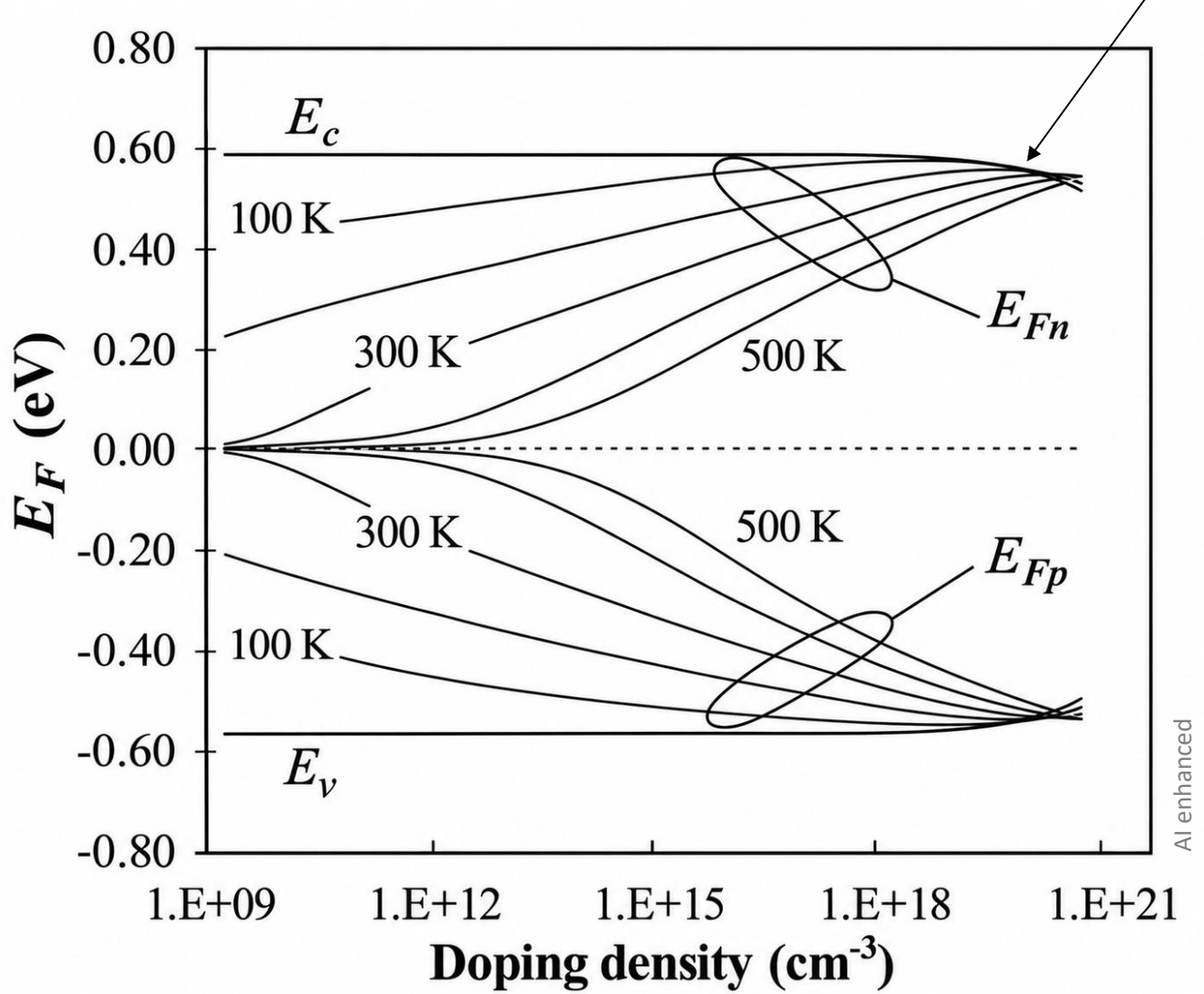
Conductivity is poor

Extrinsic: $n \neq p$

Conductivity **almost temperature independent** at room temperature

Conductivity can be strongly increased (up to a factor of 10^6)

degenerately doped semiconductor



degenerate semiconductor

Heavily doped semiconductors are called **degenerately doped**

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

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

- heavy doping narrows the band gap
- Boltzmann approximation is not valid
- degenerate semiconductors = metal