Lecture 7

4 DOPING OF SEMICONDUCTORS

4.1 Intrinsic Material

- Essentially, it is a pure crystal with no impurity atoms or defects.
- As the temperature is raised above 0 K:
  - Valence electrons in the bonds gain thermal energy
  - Some electrons in valence band gain sufficient energy to jump to conduction band become conduction of “free” electrons.
  - This process corresponds to the electrons breaking the covalent bonds leaving behind broken bonds
  - As a result, broken bonds, empty states, or holes are created.
  - The electrons and holes are created in pairs by thermal energy

- Obviously, the number of electrons in the conduction band is equal to the number of holes in the valence band.
  - The concentration of these electrons and holes is called intrinsic concentration n_i.
  - It is expected that n_i increases with increasing temperature T.

The above processes are illustrated in Fig.4.1 for silicon semiconductor.

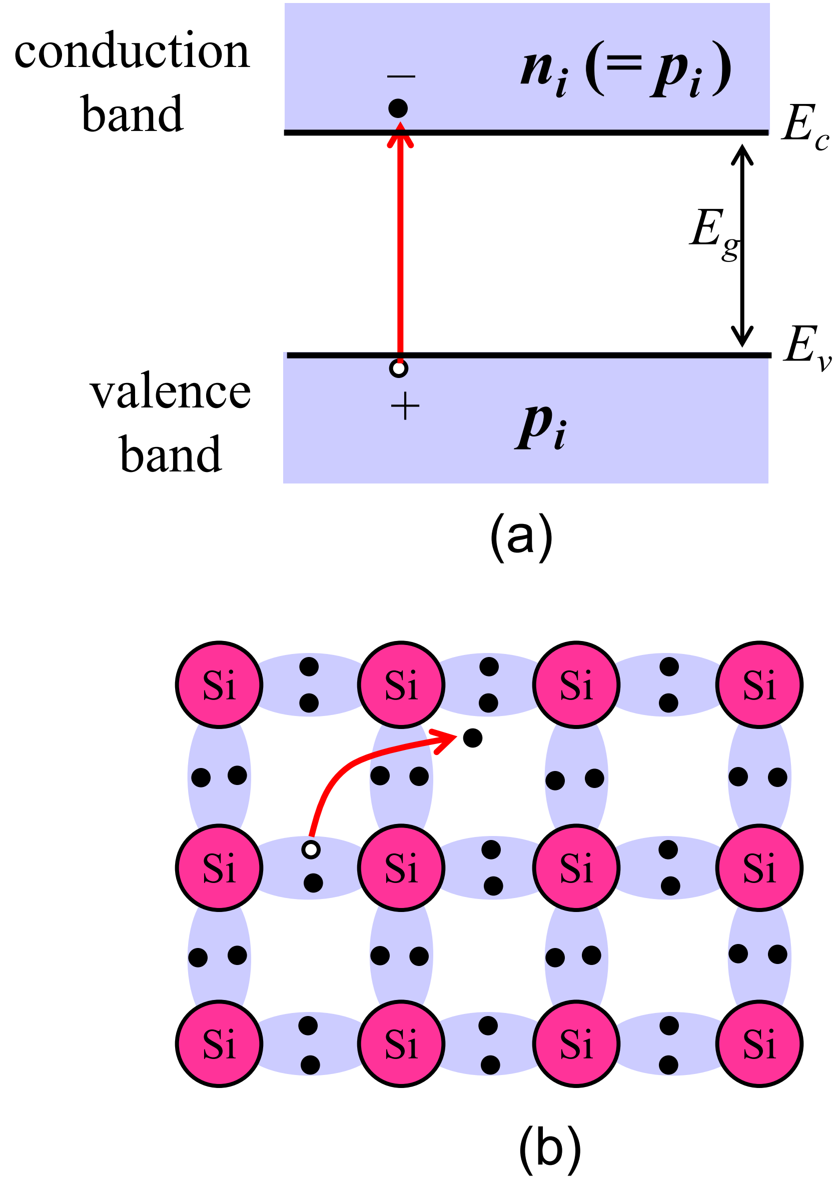


Fig..4.1

- In Silicon:

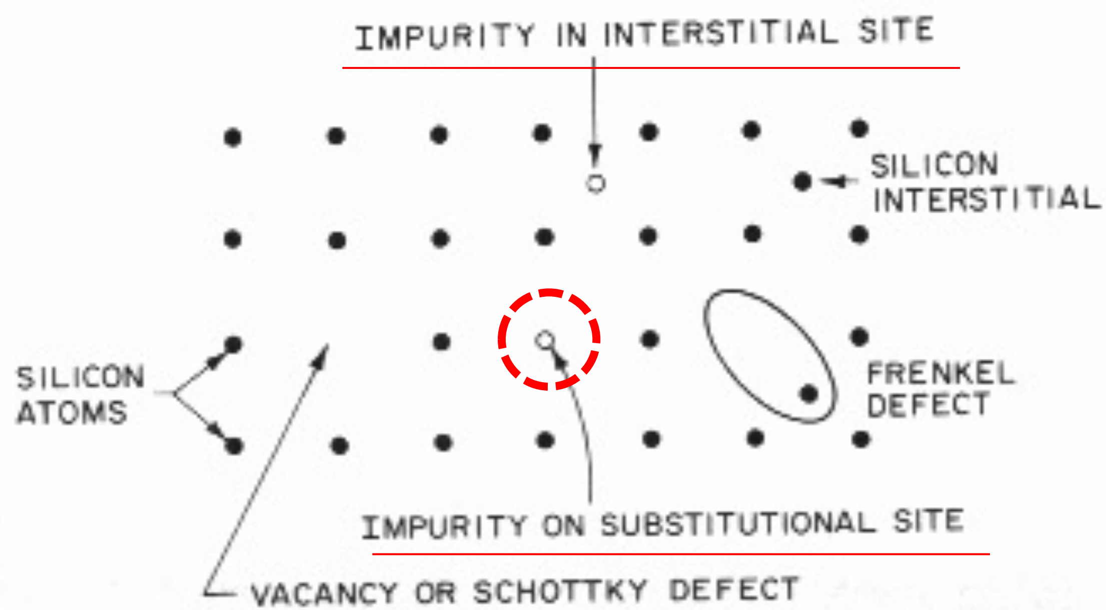
$$\text{Density of silicon atoms} = 5\times10^{22}\ \text{cm}^{-3} \text{ and}$$
$$\text{4 valence electrons per atom, so}$$
$$\text{Density of valence electrons} = 2\times10^{23}\ \text{cm}^{-3}$$

(Slides 2-45, 2-46)

- The value of n_i for silicon at 300 K is 1.5×10^{10} /cm^3
- The properties (e.g. conductivity) of the semiconductor can be changed by adding controlled amounts of specific impurity atoms, called dopant atoms, to the semiconductor crystal
- Such doped material is then called an <u>extrinsic material</u>.

4.2 Donor Impurity

- Supposing a silicon crystal is doped with impurity atoms from group V in the periodic table (e.g. P, As, Sb).
- In the crystal, the group V atoms occupy the Si atom sites, or in other words substituting or replacing the host Si atoms.



- The group V atoms in silicon crystals are called donor impurities/atoms for the reason which will be clear later.

- Consider now a group V atom, say a P atom, inside a silicon crystal (see Fig. 4.2)
  - Silicon atom has 4 valence electrons, but the phosphorus atom, P, has 5 valence electrons
  - Four valence electrons of P atom make covalent bonds with the neighboring Si atoms

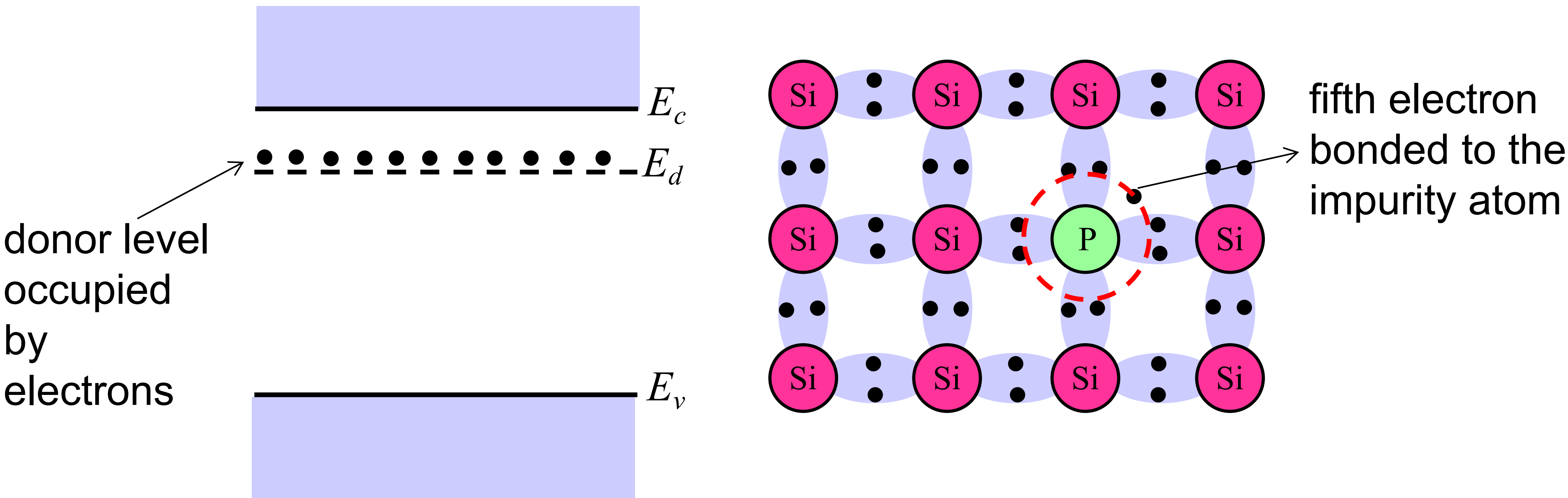
- The fifth electron is held by the P atom, but much more weakly than the other 4 electrons forming the covalent bonds with the neighboring atoms

- The binding energy of the fifth electron to the P atom can be estimated using the hydrogen atom model. It is much smaller than bandgap energy E_g (the energy necessary to break Si-Si bond to create an electron-hole pair)

- The impurity P atoms introduce an energy level E_d in the bandgap below the conduction band edge E_c. The energy level E_d is called a donor level.

- The energy difference $E_c – E_d$ corresponds to the binding energy of the fifth electron to the P atom. It is the energy required to excite an electron from the donor level to the conduction band.

- Typically, the donor levels E_d lie about 0.01 eV below E_c in Ge and about 0.03 – 0.06 eV below E_c in Si.



(a) (b)

Fig.4.2

- At 0 K, the donor level is occupied by the electrons, which corresponds to the fifth electrons being bonded to the impurity atoms.

- Above 0 K, the electrons in the donor level and the valence band gain thermal energy. The following processes occur (see Fig. 4.3):

  - Electrons from donor level are excited to the conduction band. This corresponds to the fifth electrons breaking the bonds with the impurity atoms becoming conduction electrons.

  - The impurity atoms then become positively charged or ionized. Each ionized impurity carries a charge of $+1.6 \times 10^{-19}$ C, because the initially neutral impurity atom donates one electron, the fifth electron, to the conduction band.

  - Since the impurity atoms donate the electrons to the conduction, they are called donor impurities/atoms.

  - <u>Note that in this case electrons are donated to the conduction band without creation of holes in the valence band</u>.

Table 4.1 The bandgap and ionization energies at 300 K

	Ionization energy (eV)				E_g (eV)
	Donors		Acceptors		
	P	As	B	Al	
Si	0.045	0.05	0.045	0.06	1.11
Ge	0.012	0.0127	0.0104	0.0102	0.67

- The number of electrons excited to the conduction band from the valence band (creating electron-hole pairs) is <u>much smaller</u> than those excited from the donor level, this is because the energy gap E_g is <u>much larger</u> than the energy required to excite the electrons from the donor level to the conduction band $E_c - E_d$ (see Table 4.1).
- Since the excitation of the electrons from the donor level to the conduction band ionizes the donor atoms, the energy difference $E_c - E_d$ is also called the ionization energy of the donor atoms.

As T increases slightly above 0 K,

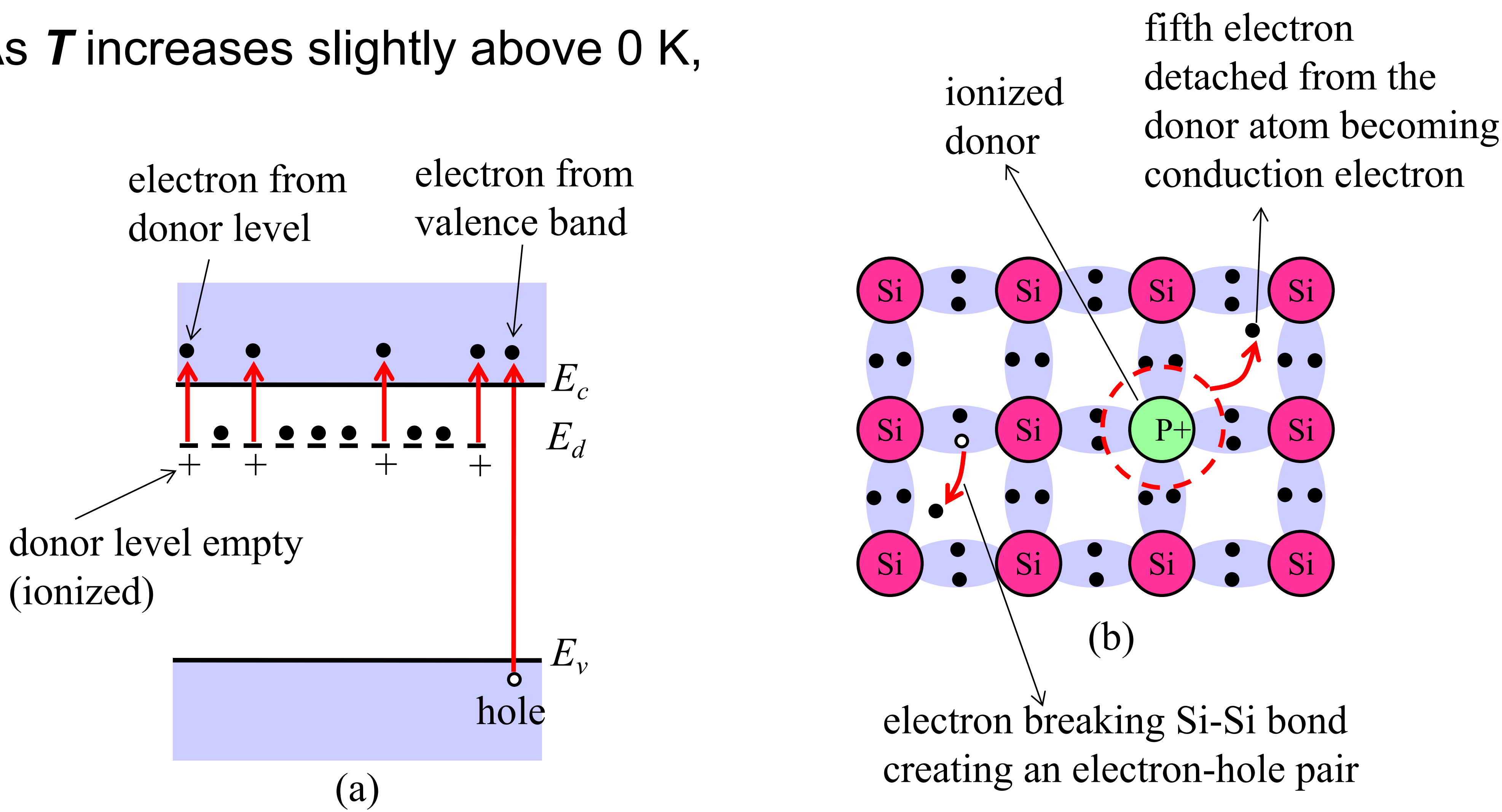
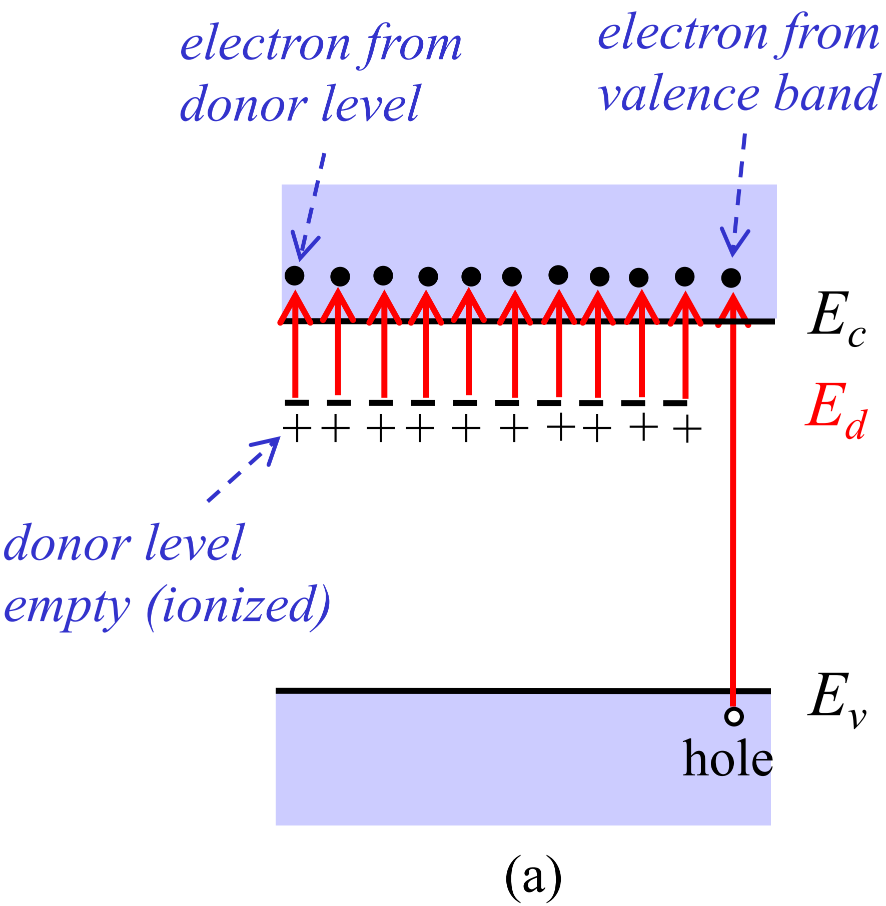


Fig.4.3

$N_d = 5\times10^{16}\ \mathrm{cm}^{-3}$

Si: $5\times10^{22}\ \mathrm{cm}^{-3}$



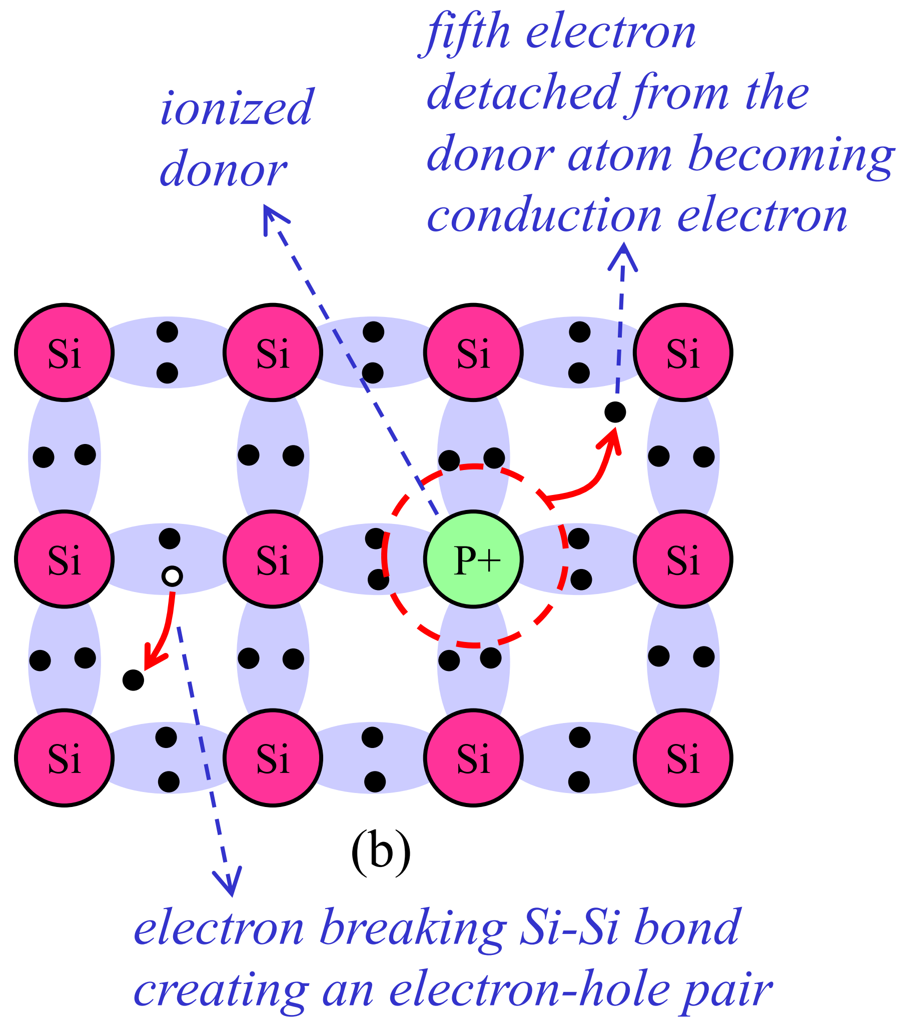


Fig.4.3a

At sufficiently high ***T*** whereby all donor impurities are ionized:

$$n_0 = N_d + p_0$$

$N_d = 5\times10^{16}$ cm^{-3}

Si: 5×10^{22} cm^{-3}

- At temperatures T whereby all the donor impurity atoms are ionized,
  - this phenomenon is called “impurity saturation (exhaustion)”

    T = 300 K (room temperature) corresponds to impurity saturation region (see Chapter 4.4)

- We can now ask a question:

  If a semiconductor is doped with donor atoms to a concentration N_d, what is the thermal equilibrium electron concentration in the conduction band n_0 at temperature T whereby all the donor impurity atoms are ionized?

- The thermal equilibrium electron concentration in the conduction band n_0 is the sum of

  - Electron concentration excited from the donor level to the conduction band. This electron concentration is equal to the donor concentration N_d since all donor impurity atoms are ionized. And consequently, all the donor impurities become positive ions.

  - Electron concentration excited from the valence band to the conduction band. This electron concentration is equal to the hole concentration in the valence band p_0 since they are created in pairs.

  Mathematically, we write:

$$\underbrace{n_0}_{\text{negative charge concentration}} = \underbrace{N_d + p_0}_{\text{positive charge concentration}} \qquad \textbf{(4.1)}$$

- The total charge concentration at thermal equilibrium is zero.
- We have established here the charge neutrality condition at thermal equilibrium.

- The positively charged ionized donor atoms are fixed in the crystal (covalently bonded with the neighboring atoms).
- They play important roles in the operation of devices, but do not participate in the electrical conduction.
- The electrical conduction in semiconductors is carried out by electrons and holes only.

- In the presence of donor atoms, the electrons from the donor atoms are donated to the conduction band without the creation of holes. It follows that

$$n_0 > p_0$$

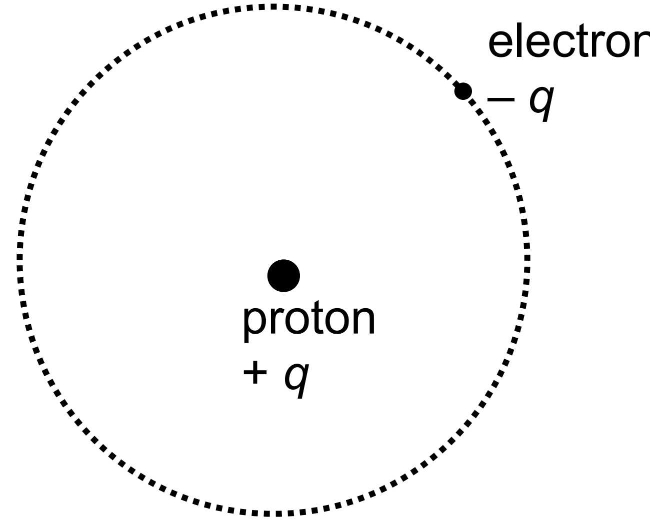
This type of semiconductor, where $n_0 > p_0$, is called n-type semiconductor,

  - the electrons are referred to as majority carriers and
  - the holes are referred to as minority carriers

Example 4.1

Estimate the donor binding energy for GaAs, given that the effective mass of electron $m_n^* = 0.067\ m_0$ and the relative permitivity ε_r of GaAs is 13.2

For hydrogen atom, the electron energy is [see Appendix A, eqn. (A.3.b)]



$$E_n = -\frac{q^4}{2(4\pi\ \hbar)^2}\left(\frac{m_0}{\varepsilon_0{}^2}\right)\frac{1}{n^2} = -\frac{13.6}{n^2}\ \text{eV} \qquad (4.2)$$

$n = 1, 2 \ldots\ldots\ldots\ldots \infty$

Fig.4.4

here, m_0 is the electron rest mass
and ε_0 is the permitivity of free space or vacuum

The donor atom with its donor electron in GaAs resembles the hydrogen atom. Therefore, we can estimate the donor electron energy using eqn. (4.2), but with the following modification:

- use the electron effective mass $m_n^* = 0.067\ m_0$ instead of electron rest mass m_0
- use and permitivity of GaAs $\varepsilon = \varepsilon_r\ \varepsilon_0 = 13.2\ \varepsilon_0$ instead of permitivity of free space ε_0

Eqn. (4.2) becomes

$$E_n = -\frac{q^4}{2(4\pi\ \hbar)^2}\left(\frac{m_n^*}{\varepsilon_r^{\ 2}\varepsilon_0^{\ 2}}\right)\frac{1}{n^2} \tag{4.3}$$

$$E_n = -\left(\frac{0.067}{13.2^2}\right)\frac{13.6}{n^2} = -\frac{0.0052}{n^2}\ \text{eV} \tag{4.4}$$

for $n = 1$, $E_1 = -0.0052\ \text{eV}$

for $n = \infty$, $E_\infty = 0$

The energy required to excite the electron from the ground state (n = 1) to the free state ($n = \infty$) is

$$E_\infty - E_1 = 0.0052 \text{ eV} \qquad (4.5)$$

which corresponds to the energy difference $E_c - E_d$, the ionization energy or the binding energy.

Key takeaways (Lecture #7)

- Intrinsic semiconductor:
  - number of electrons in the conduction band = number of holes in the valence band
  - n_i increases with increasing temperature T
- Extrinsic semiconductor:
  - The properties (e.g. conductivity) of the semiconductor can be changed by adding controlled amounts of specific impurity atoms, called dopant atoms
  - Group V (such as Phosphorous, P) atoms in silicon crystals are called donor impurities/atoms
  - Electrons are donated to the conduction band without creation of holes in the valence band

$$n_0 = N_d + p_0$$

  - Since $n_0 > p_0$, this semiconductor is called n-type semiconductor

Lecture 8

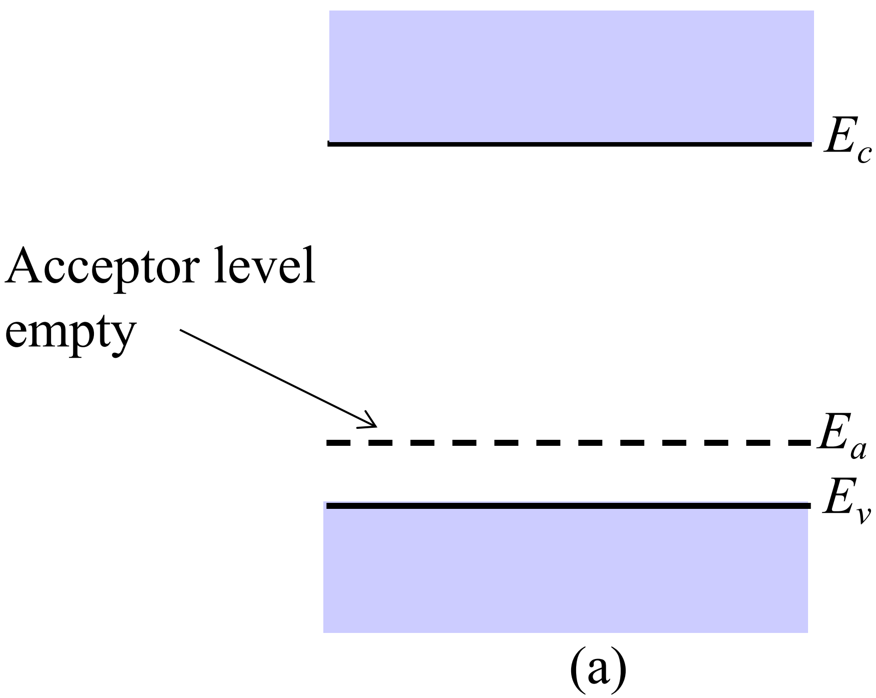
4.3 Acceptor Impurity

- We will now consider a situation where a silicon crystal is doped with impurity atoms from group III in the periodic table (e.g. B, Al, Ga).

- The group III atoms substitute the host Si atoms. The group III atoms in silicon crystals are called acceptor impurities/atoms, the reason will be clear later

- Consider now a group III atom, say a B atom, inside a silicon crystal (see Fig. 4.5)
  - Silicon atom has 4 valence electrons, but the boron atom, B, has only 3 valence electrons
  - In making covalent bonding with the neighboring Si atoms, the B atom only contributes 3 electrons thereby leaving one incomplete bond.
  - The impurity B atom introduces an energy level E_a in the energy gap above the valence band edge E_v. This energy level is called an acceptor level.
  - The energy difference $E_a - E_v$ is the energy required to excite an electron from the valence band to the acceptor level.
  - This corresponds to the electron from the Si-Si covalent bond to move to the incomplete Si-B bond. The energy difference $E_a - E_v$ is much smaller than the bandgap energy E_g.

- In Si, the acceptor levels E_a generally lie about 0.03-0.06 eV above E_v, whereas in Ge, the the acceptor levels lie about 0.01 eV above E_v
- At 0 K, the acceptor level is empty. This corresponds to the incomplete Si-B covalent bond.



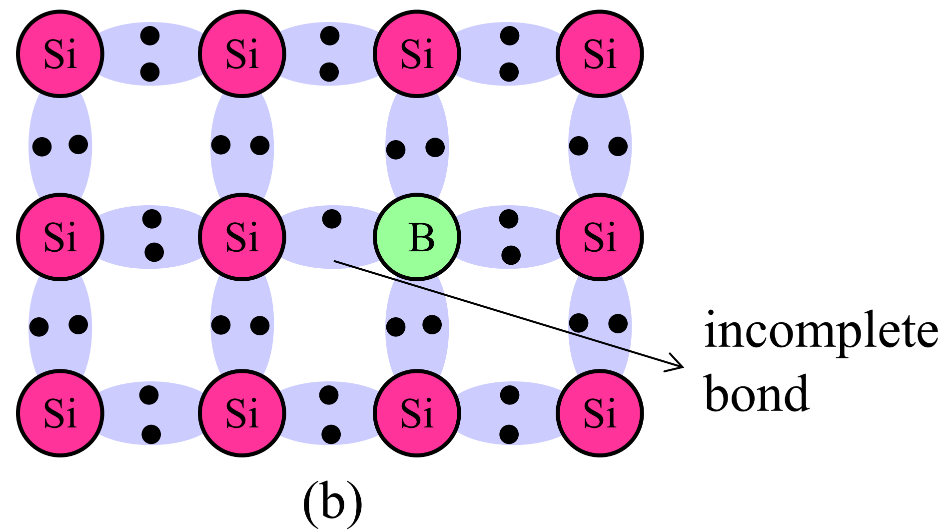


Fig.4.5

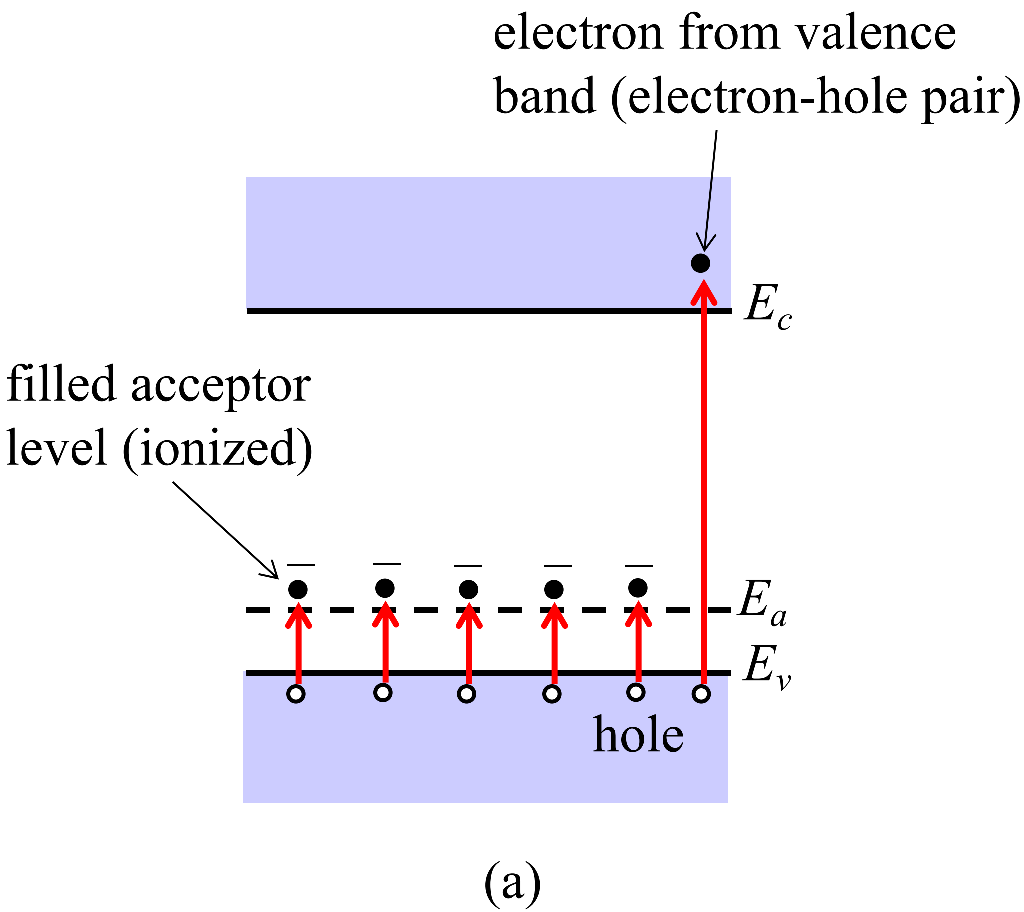
- Above 0 K, the electrons in the valence band gain thermal energy. The following processes occur (see Fig. 4.6):
    - Some electrons from the valence band are excited to the acceptor level creating holes in the valence band.
    - This corresponds to the electrons from the Si-Si bonds move occupying the incomplete Si-B bonds.
    - The impurity B atoms then become negatively charged or ionized. Each ionized impurity carries a charge of -1.6×10^{-19} C, because the initially neutral impurity atom accepts one electron from the valence band.
    - Since the impurity atoms accept electrons, they are called acceptor impurities.
    - <u>Note that in this case holes are created in the valence band without creation of electrons in the conduction band.</u>

Table 4.1 The bandgap and ionization energies at 300 K

	Ionization energy (eV)				E_g (eV)
	Donors		Acceptors		
	P	As	B	Al	
Si	0.045	0.05	0.045	0.06	1.11
Ge	0.012	0.0127	0.0104	0.0102	0.67

- Relatively much smaller number of electrons from the valence band are excited to the conduction band creating electron-hole pairs, simply because the energy gap E_g is much larger than the energy required to excite the electrons from the valence band to the acceptor level $E_a - E_v$ (see Table 4.1)

- Here, the ionization energy of the acceptor atoms is the energy difference $E_a - E_v$



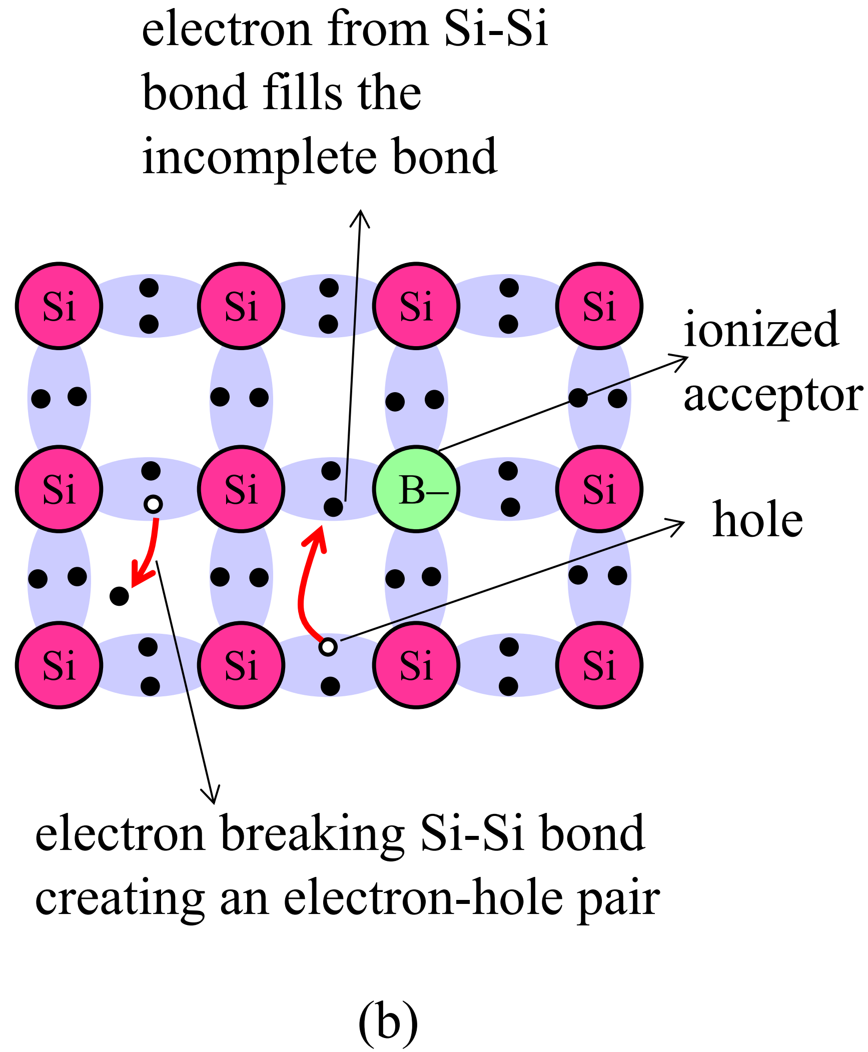


Fig.4.6

At ***T* > 0 K** whereby all acceptor impurities are ionized:

$$p_0 = N_a + n_0$$

- Consider the situation at temperatures T whereby all the acceptor impurity atoms are ionized.
  - The semiconductor enters the impurity saturation (exhaustion) region (see section 4.4).
  - If the acceptor atom concentration is N_a, the thermal equilibrium hole concentration in the valence band p_0 at T is the sum of
    - hole concentration due to the excitation of electron from the valence band to the acceptor level. This hole concentration is equal to the acceptor atom concentration N_a since all acceptor impurities are ionized. And consequently, all acceptor impurities become negative ions.
    - hole concentration due to the excitation of electrons from the valence band to the conduction band. This hole concentration is equal to the electron concentration in the conduction band n_0 since they are created in pairs.

- Mathematically, we write:

$$\underbrace{p_0}_{\text{positive charge concentration}} = \underbrace{N_a + n_0}_{\text{negative charge concentration}} \qquad \textbf{(4.6)}$$

- Again, eqn. (4.6) satisfies the charge neutrality condition.
- In Chapter 5 we will use the charge neutrality condition to calculate the thermal equilibrium electron and hole concentrations when donor, acceptor or both impurities are present.

- In the presence of acceptor concentration, holes in the valence band are created without the creation of electrons in the conduction band, and therefore

$$p_0 > n_0$$

This type of semiconductor, where $p_0 > n_0$, is called p-type semiconductor,

  - the holes are referred to as majority carriers and
  - the electrons are referred to as minority carriers

4.4 Temperature dependence of carrier concentration

Fig. 4.7 shows the thermal equilibrium majority carrier concentration of an n-type semiconductor as a function of temperature *T*.

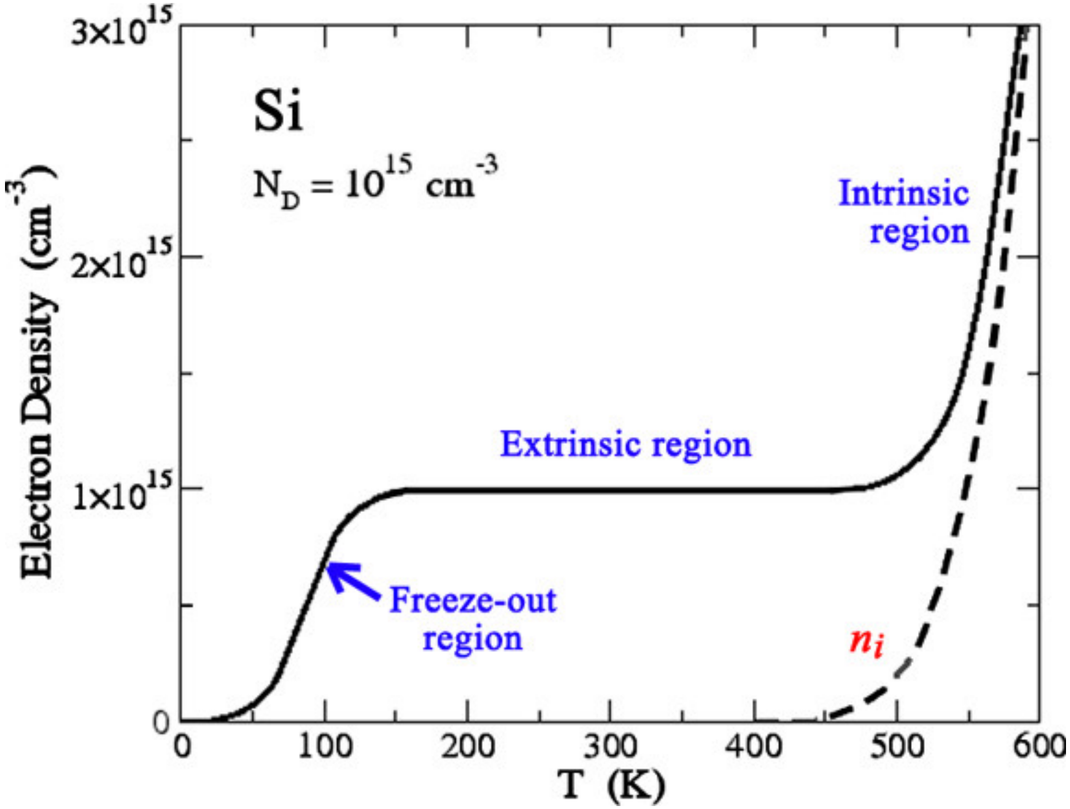


Fig. 4.7

- At 0 K, there is no excitation of electrons from the donor level and the valence band to the conduction band (see Fig. 4.2). Hence, the electron and hole concentrations are both zero.

- From 0 K to ~ 150 K, the electron concentration in the conduction band increases. Above 0 K, the electrons gain thermal energy and the following processes occur (see also Fig. 4.3) .

  - Electrons at the donor level are excited to the conduction band

  - There are some electrons excited from the valence band to the conduction band creating the electron-hole pairs. The number of these electrons are much smaller than those from the donor level because the energy gap E_g is much larger than $(E_c – E_d)$.

- From about 150 K to 450 K, the electron concentration is nearly constant. The reason is that the donor atoms are fully ionized and, yet, at this temperature range the electrons excited from the valence band to the conduction band, creating electron-hole pairs, are still much smaller than those excited from the donor level.

- Above 450 K, the electron concentration increases sharply. This corresponds to the increasing number of electrons being excited from the valence band to the conduction band creating electron-hole pairs. Here, the number of electrons from the donor level remain constant since the donor atoms have been fully ionized.

- As the electron-hole pair concentration increases and becomes much larger than the donor concentration, the semiconductor reverts to an intrinsic semiconductor.

- For fully ionized donor impurities, we can also see the variation of the electron concentration with temperature from eqn. (4.1)

$$\underbrace{n_0}_{\text{negative charge concentration}} = \underbrace{N_d + p_0}_{\text{positive charge concentration}} \qquad \textbf{(4.1)}$$

- At about 150 K to 450 K, where the electron concentration is approximately constant

$$p_0 << N_d$$

$$\therefore n_0 \approx N_d$$

- Above 450 K, where the electron concentration increases sharply

$$p_0 \gg N_d$$

$$\therefore n_0 \approx p_0 \longrightarrow \text{intrinsic semiconductor}$$

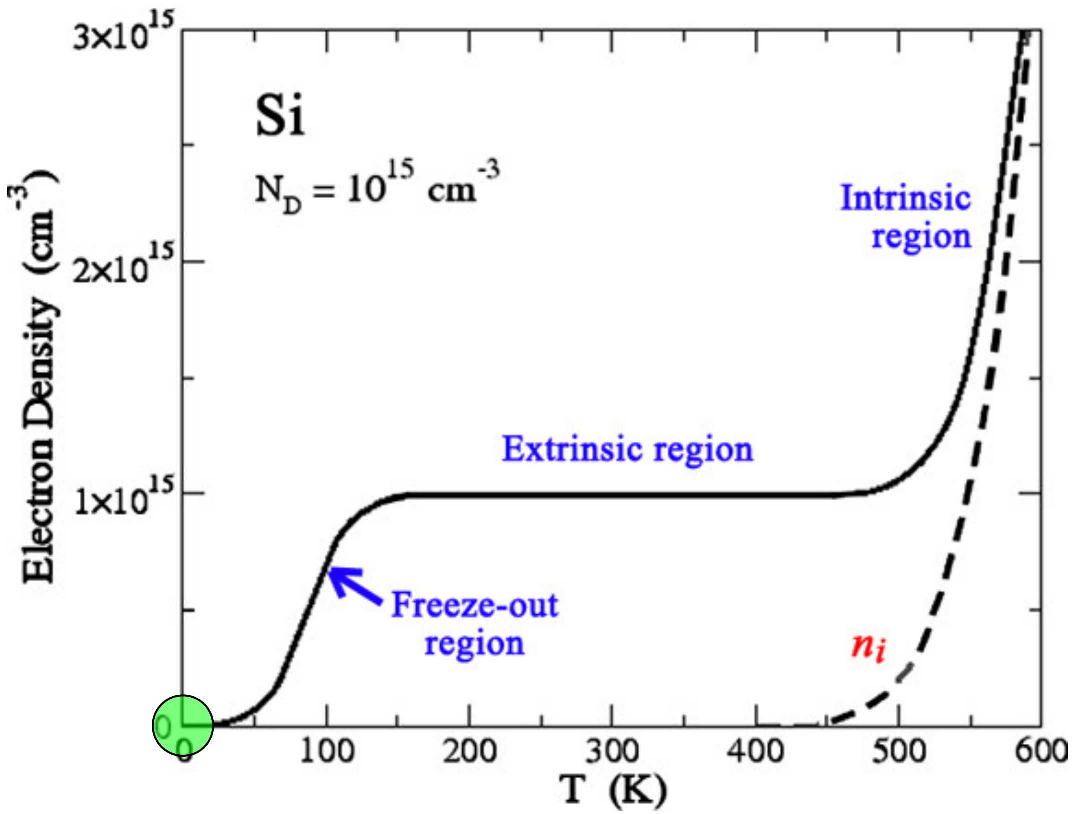
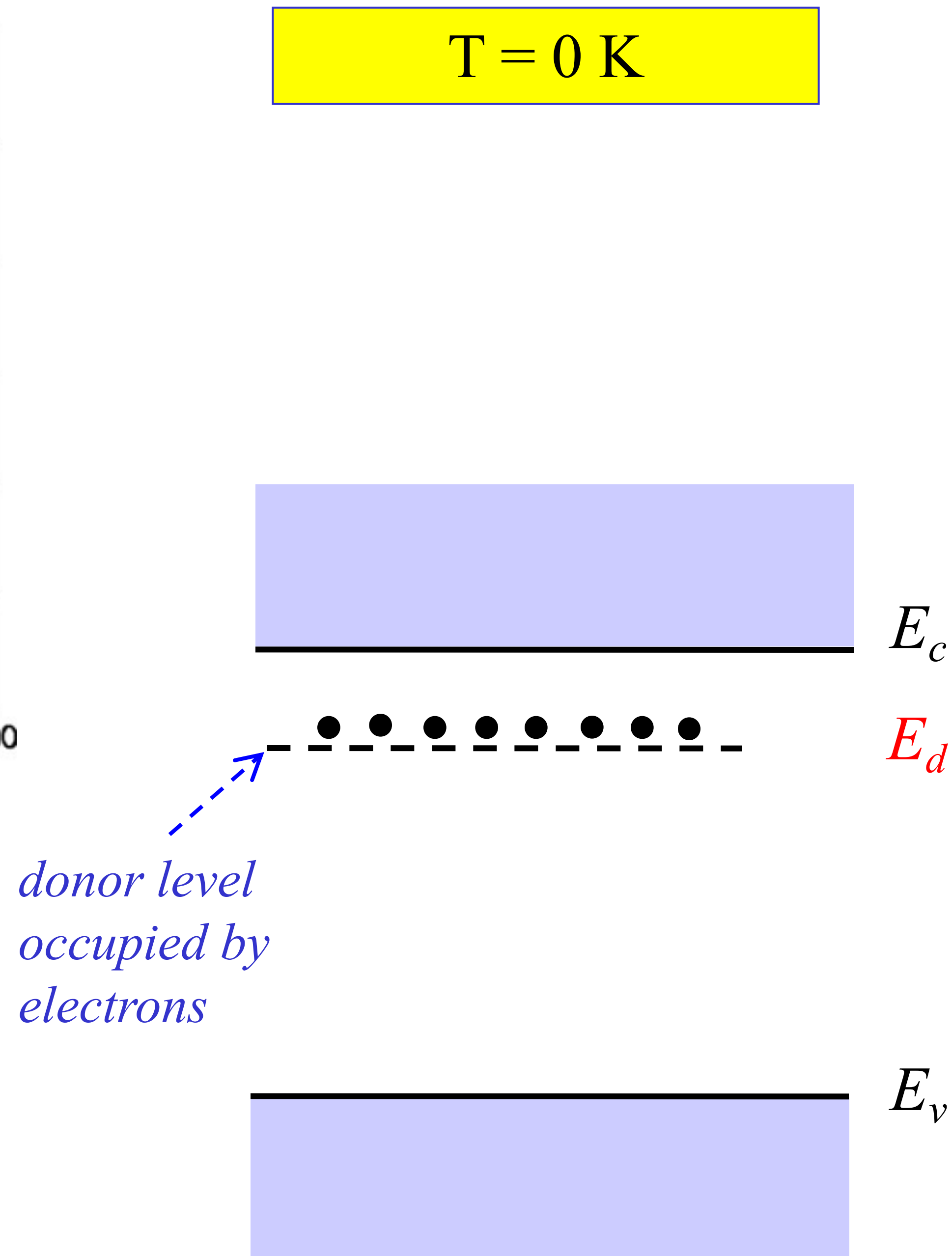

Si
N_D = 10^15 cm^-3
Intrinsic region
Extrinsic region
Freeze-out region
n_i
Electron Density (cm^-3)
T (K)
0
100
200
300
400
500
600
3×10^15
2×10^15
1×10^15

Fig. 4.7


T = 0 K
E_c
E_d
E_v
donor level occupied by electrons

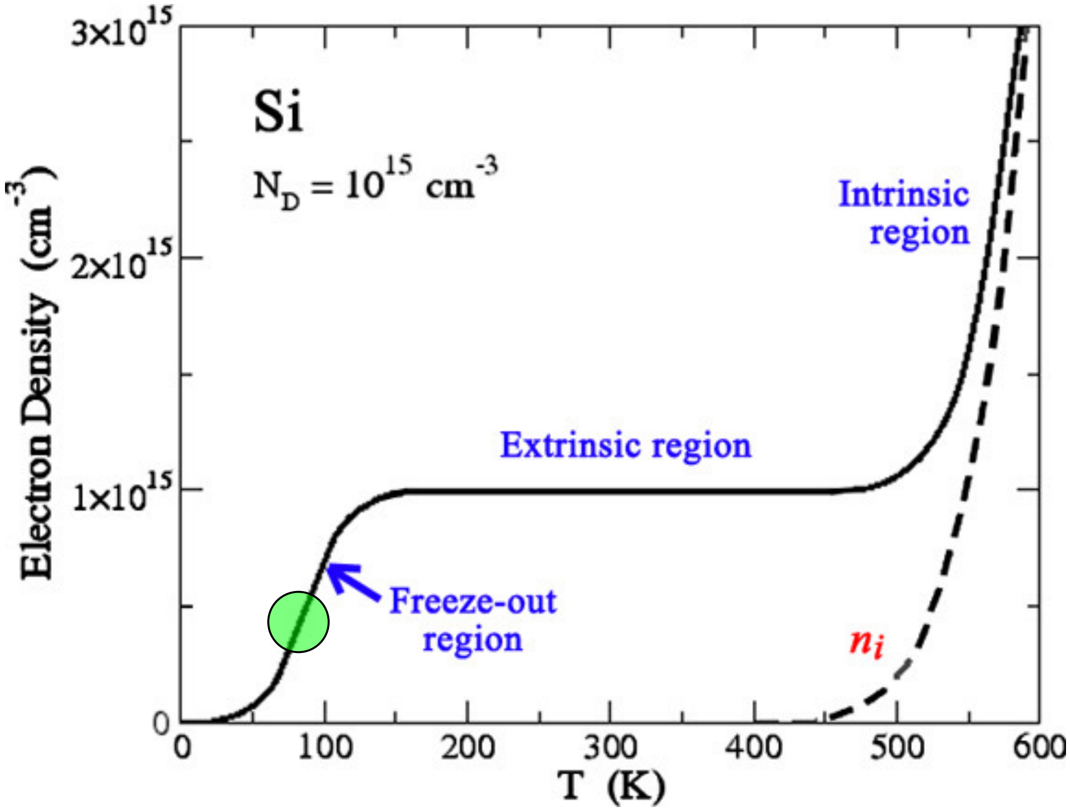
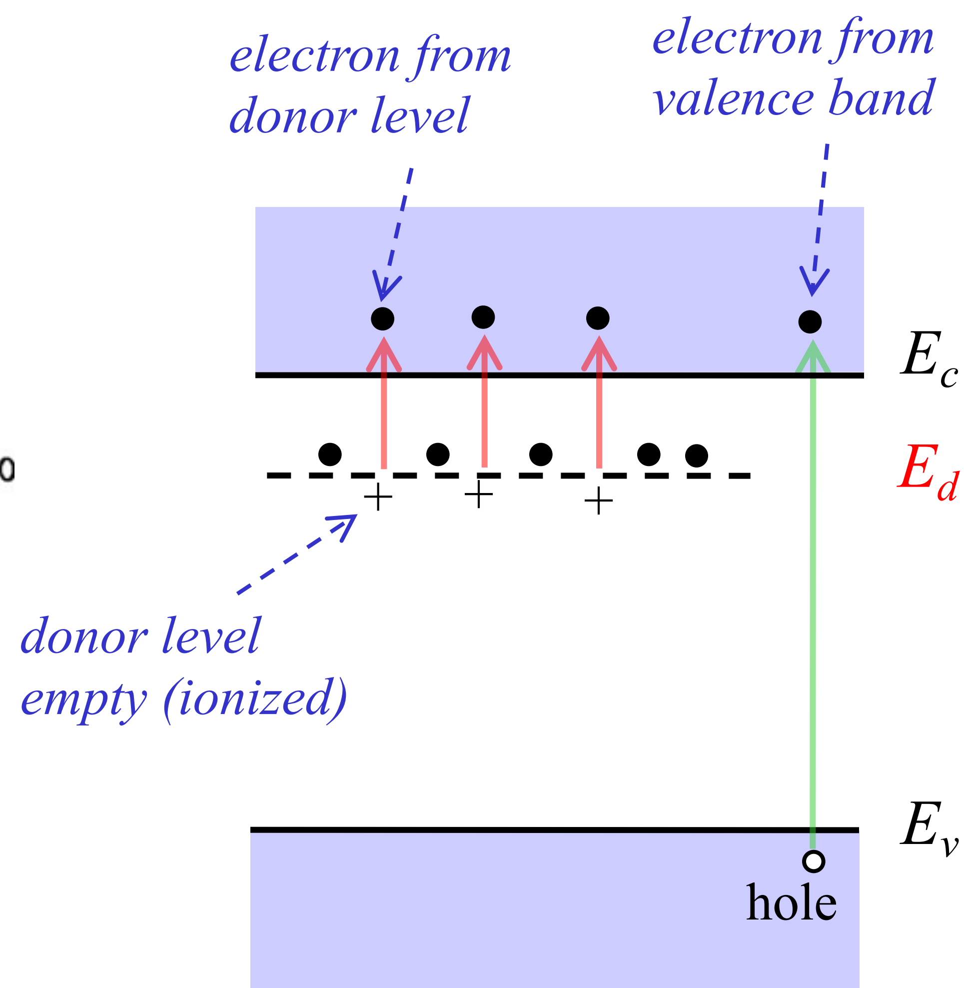


Fig. 4.7

0 K < T < 150 K

$$n_0 = N_d^+ + p_0$$



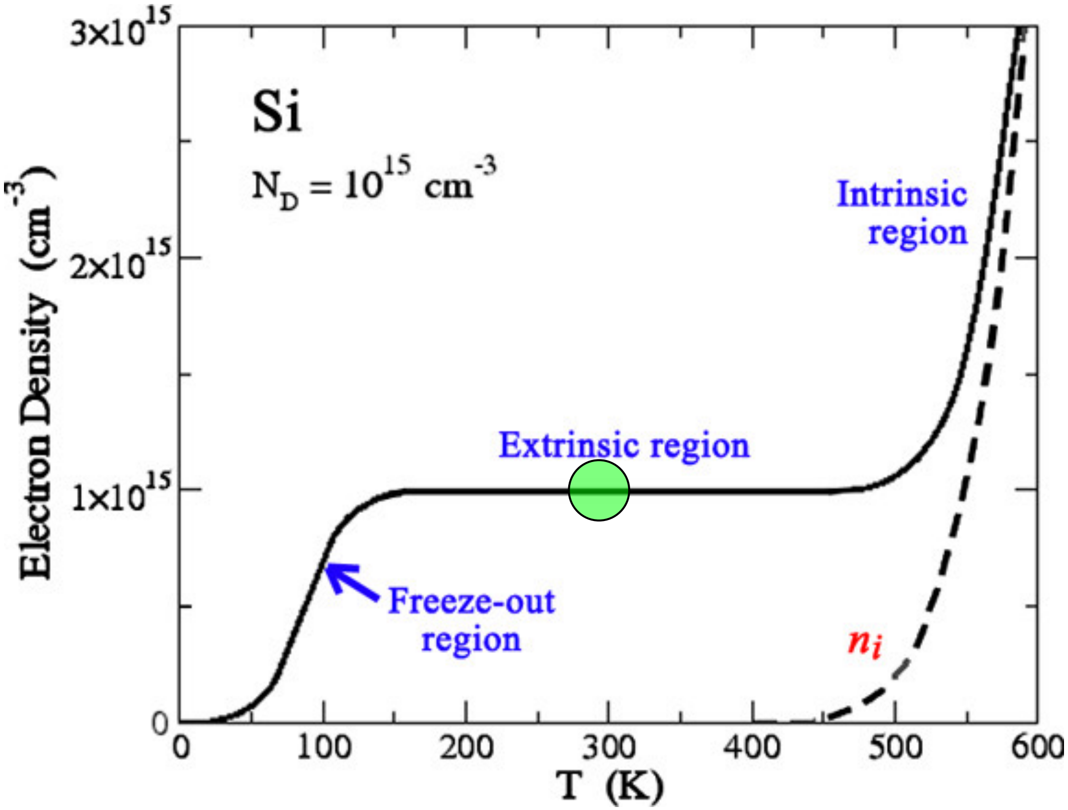


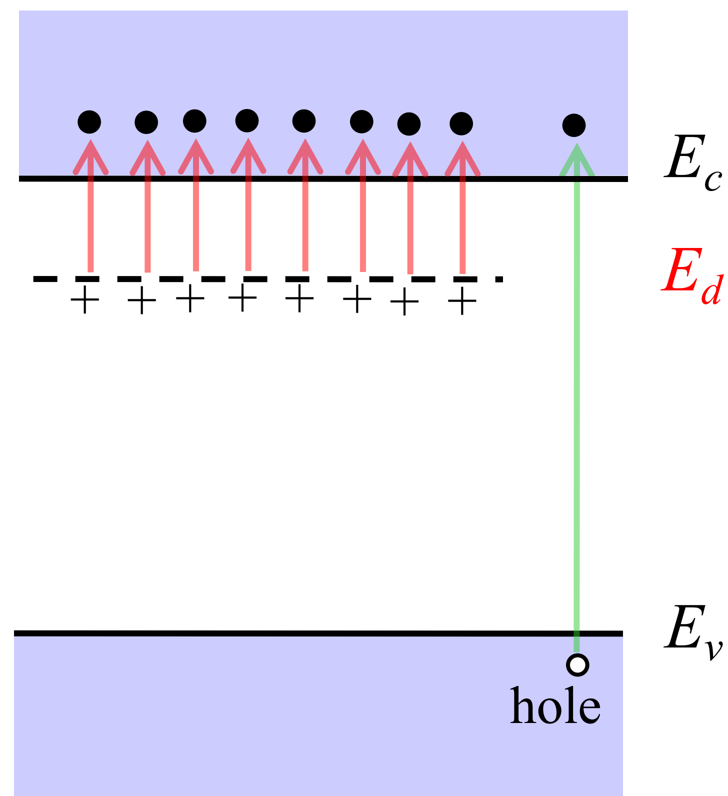
Fig. 4.7

150 K < T < 450 K

$$n_0 = N_d + p_0$$

$$N_\mathrm{d} >> p_0$$

$$n_0 \approx N_\mathrm{d}$$



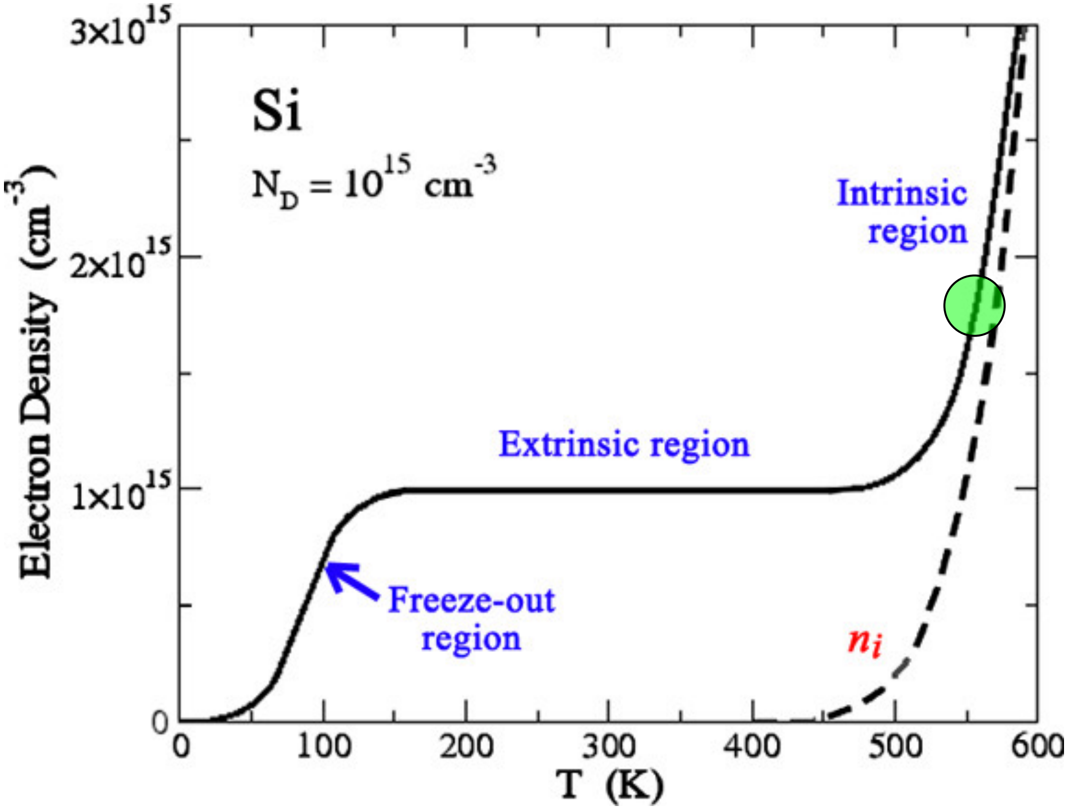


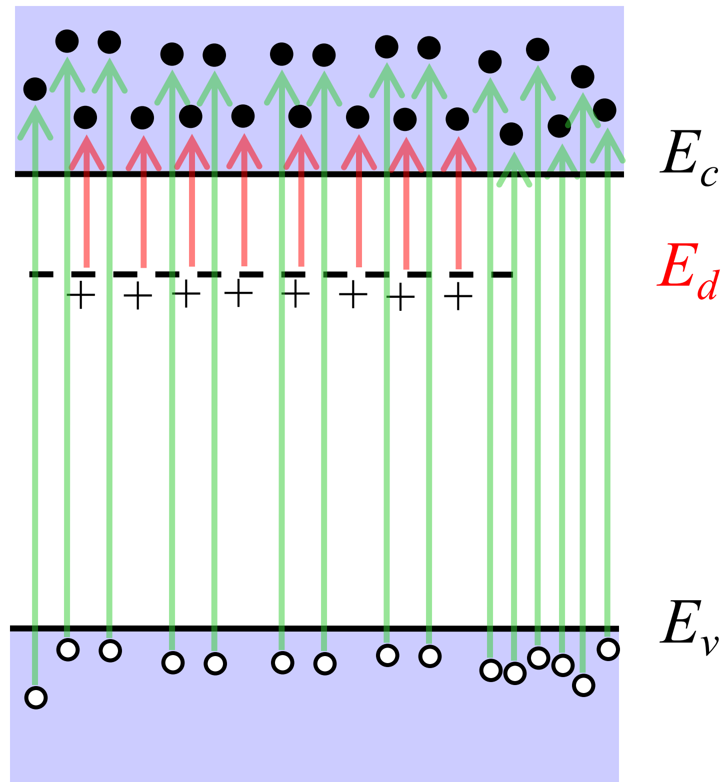
Fig. 4.7

T > 450 K

$$n_0 = N_d + p_0$$

$$N_\mathrm{d} << p_0$$

$$n_0 \approx p_0$$

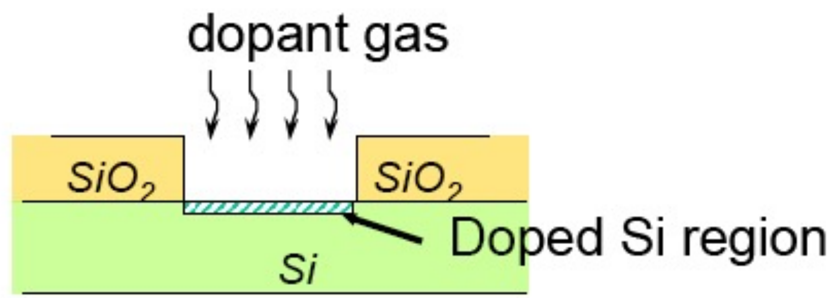


Doping Technology
(not required for exam)

(1) Diffusion

(1) Predeposition

dose control



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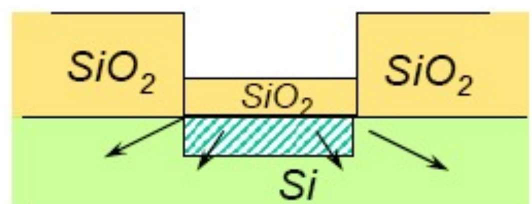
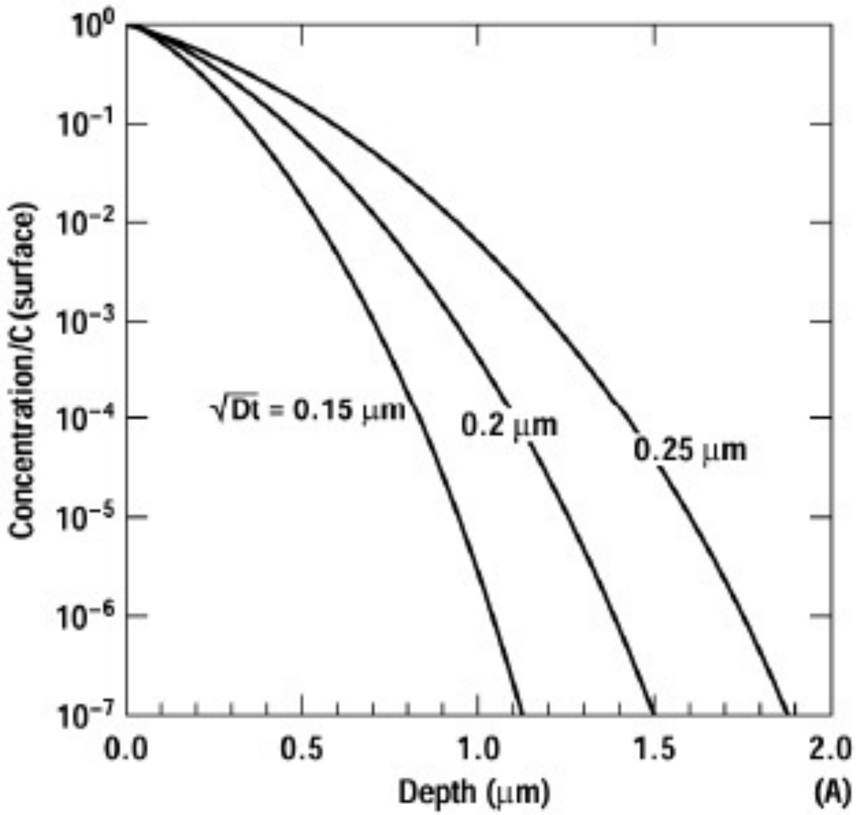
(2) Drive-in

Turn off dopant gas
or seal surface with oxide

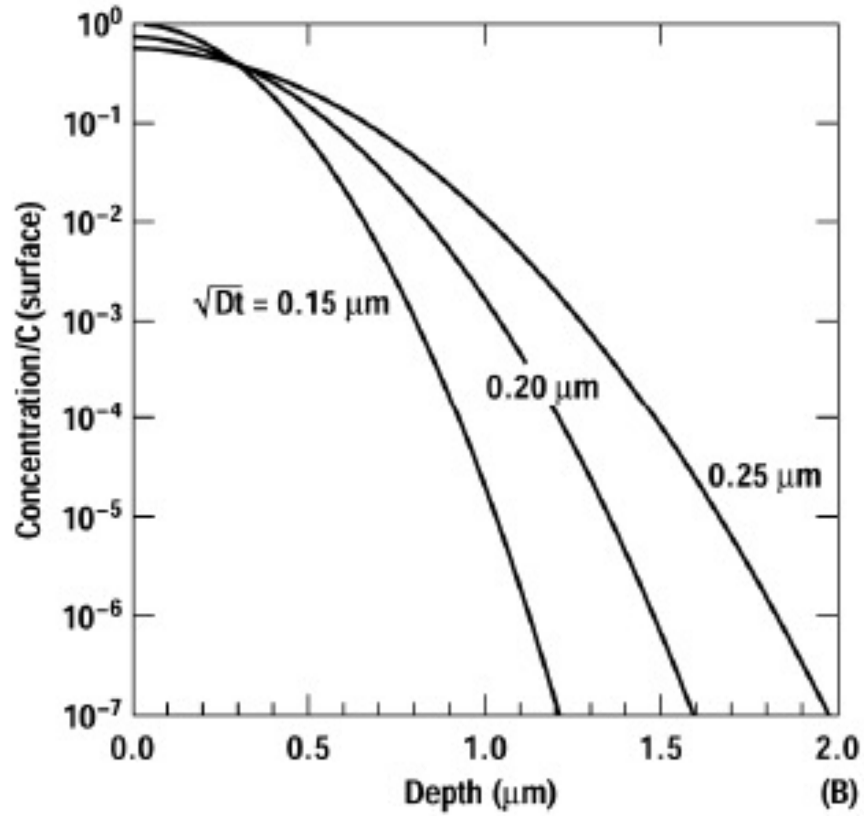
profile control
(junction depth;
concentration)



Doping profiles

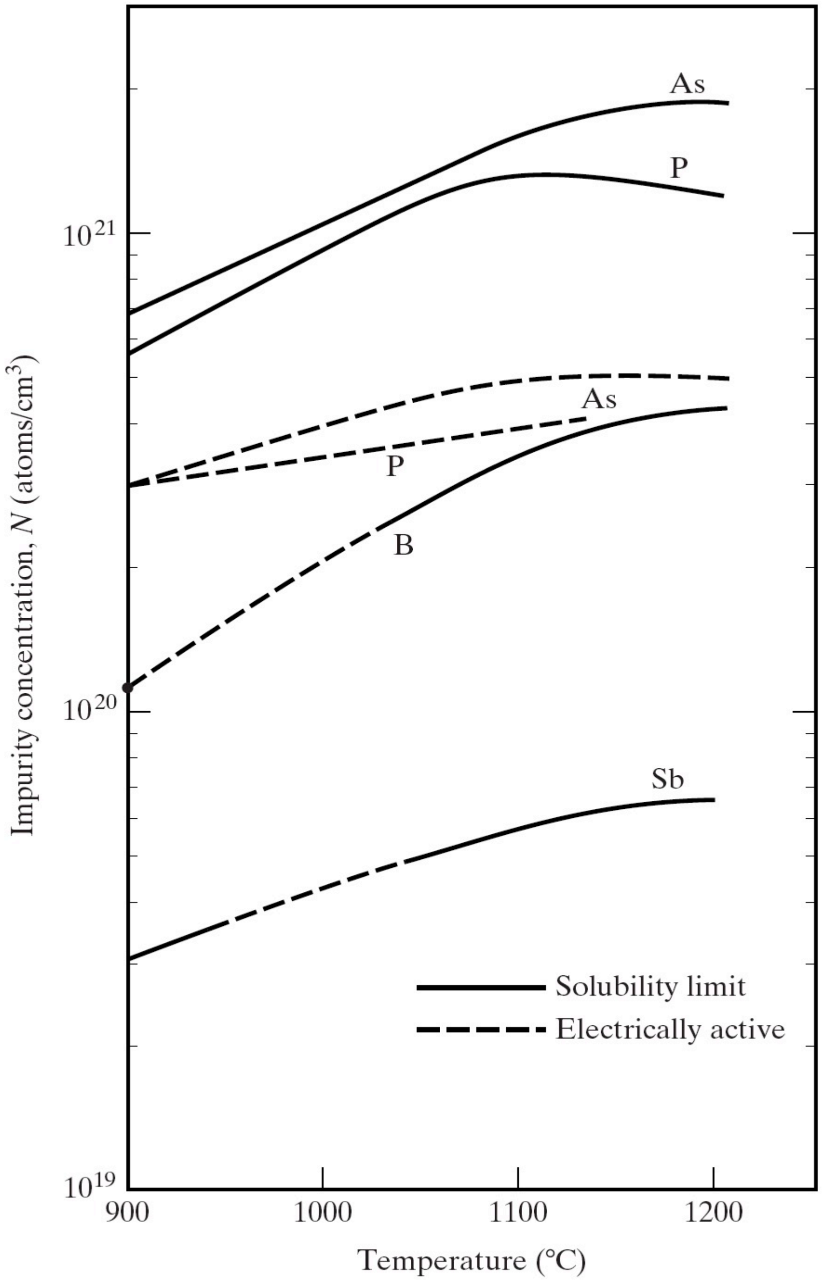


Pre-deposition



Drive-in

Diffusion - Solid Solubility Limits

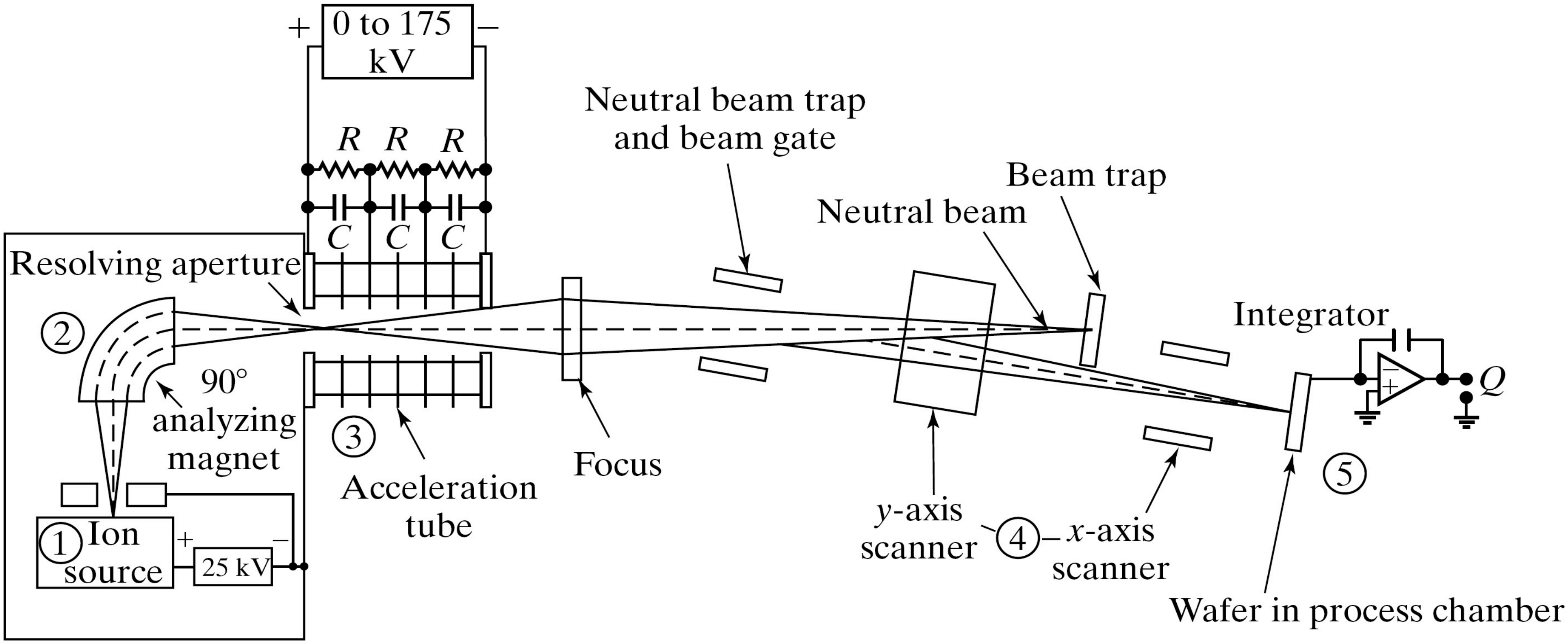


- There is a limit to the amount of a given impurity that can be “dissolved” in silicon (the Solid Solubility Limit)
- At high concentrations, all of the impurities introduced into silicon will not be electrically active

FIGURE 4.6

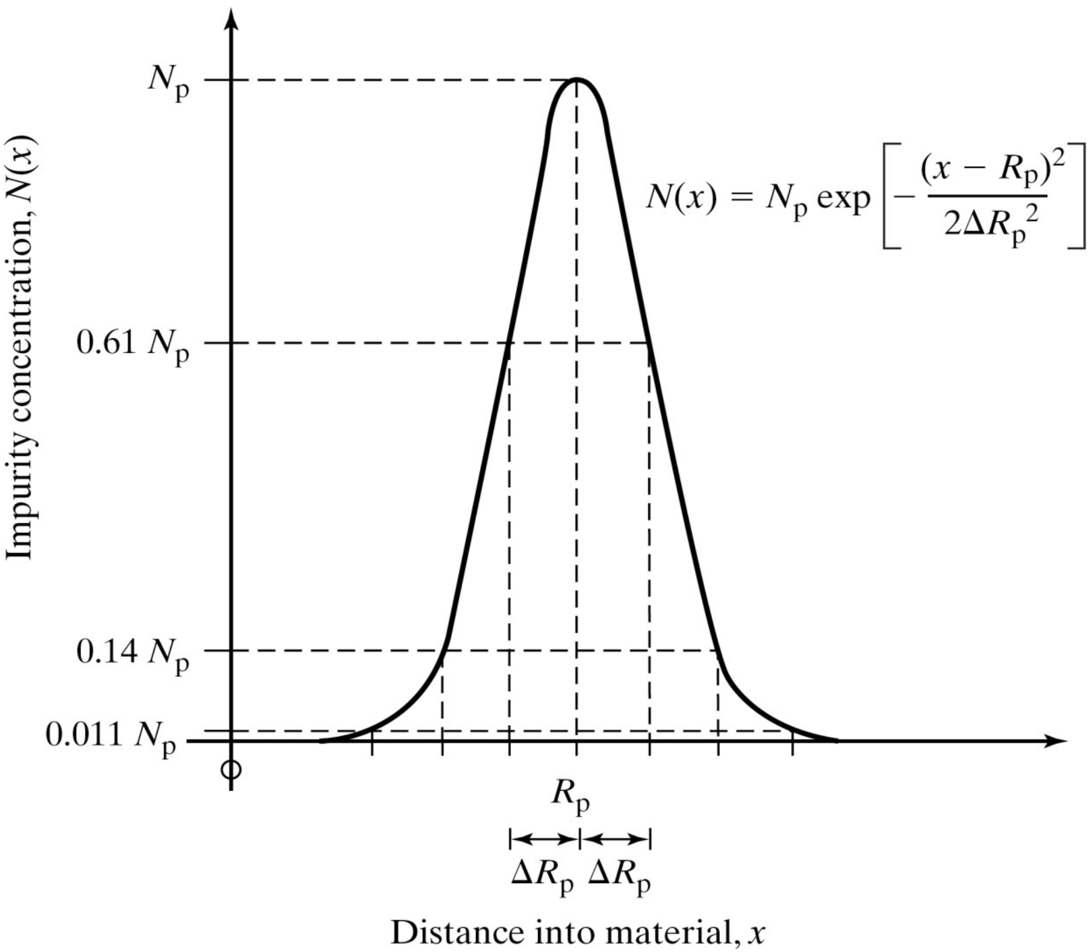
The solid-solubility and electrically active impurity-concentration limits in silicon for antimony, arsenic, boron, and phosphorus. Reprinted with permission from Ref. [29]. This paper was originally presented at the 1977 Spring Meeting of The Electrochemical Society, Inc., held in Philadelphia, Pennsylvania.

(2) Ion implantation



- Ion implantation
- Rapid annealing

Ion Implantation
Mathematical Model



Gaussian Profile

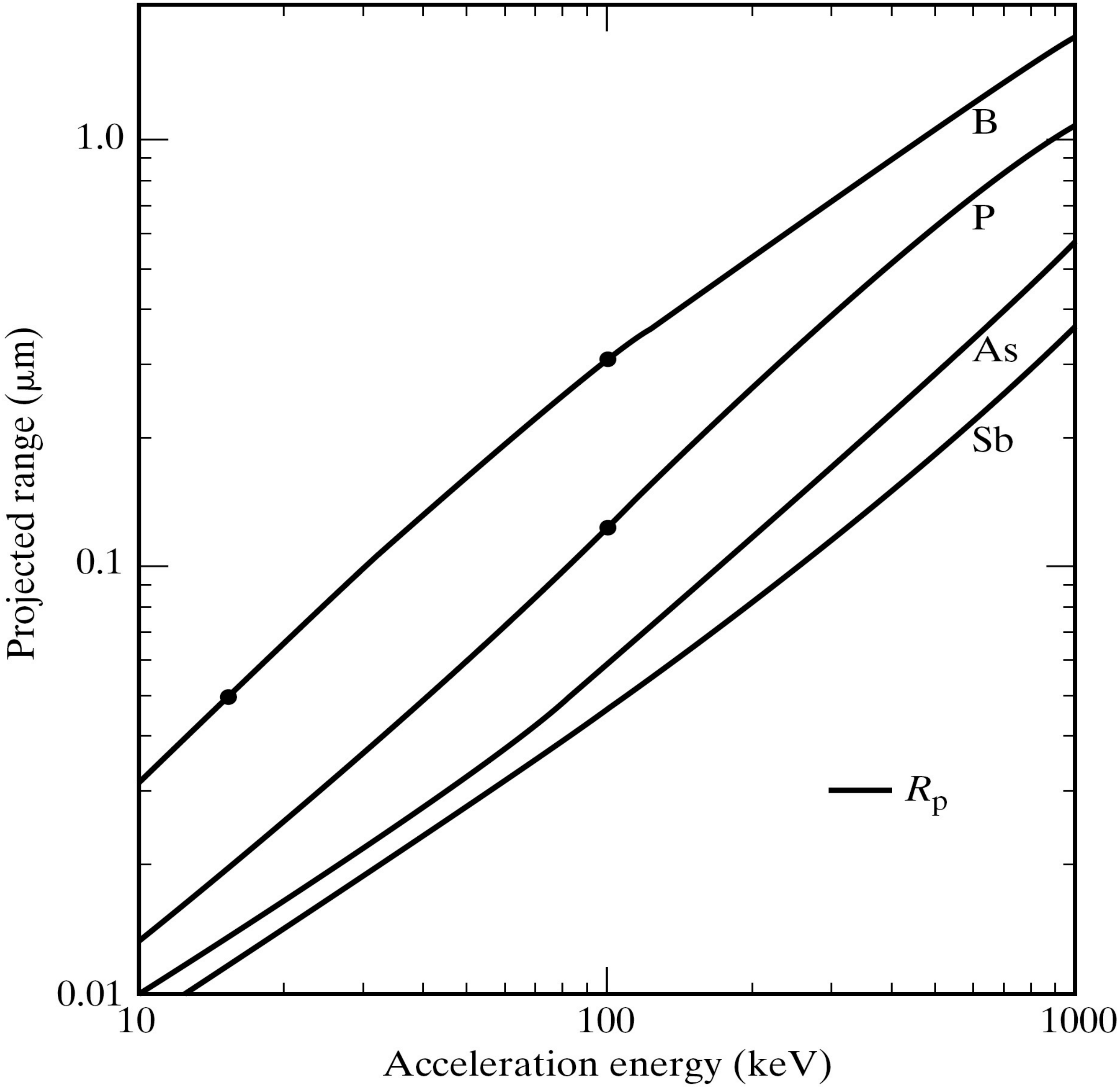
$$N(x) = N_p \exp\left[-\frac{(x-R_p)^2}{2\Delta R_p^2}\right]$$

R_p = Projected Range

ΔR_p = Straggle

Dose $\quad Q = \int_0^\infty N(x)dx = \sqrt{2\pi} N_p \Delta R_p$

Projected Range



(a)

10.8
31.0
74.9
121.8

Resistivity vs. Doping

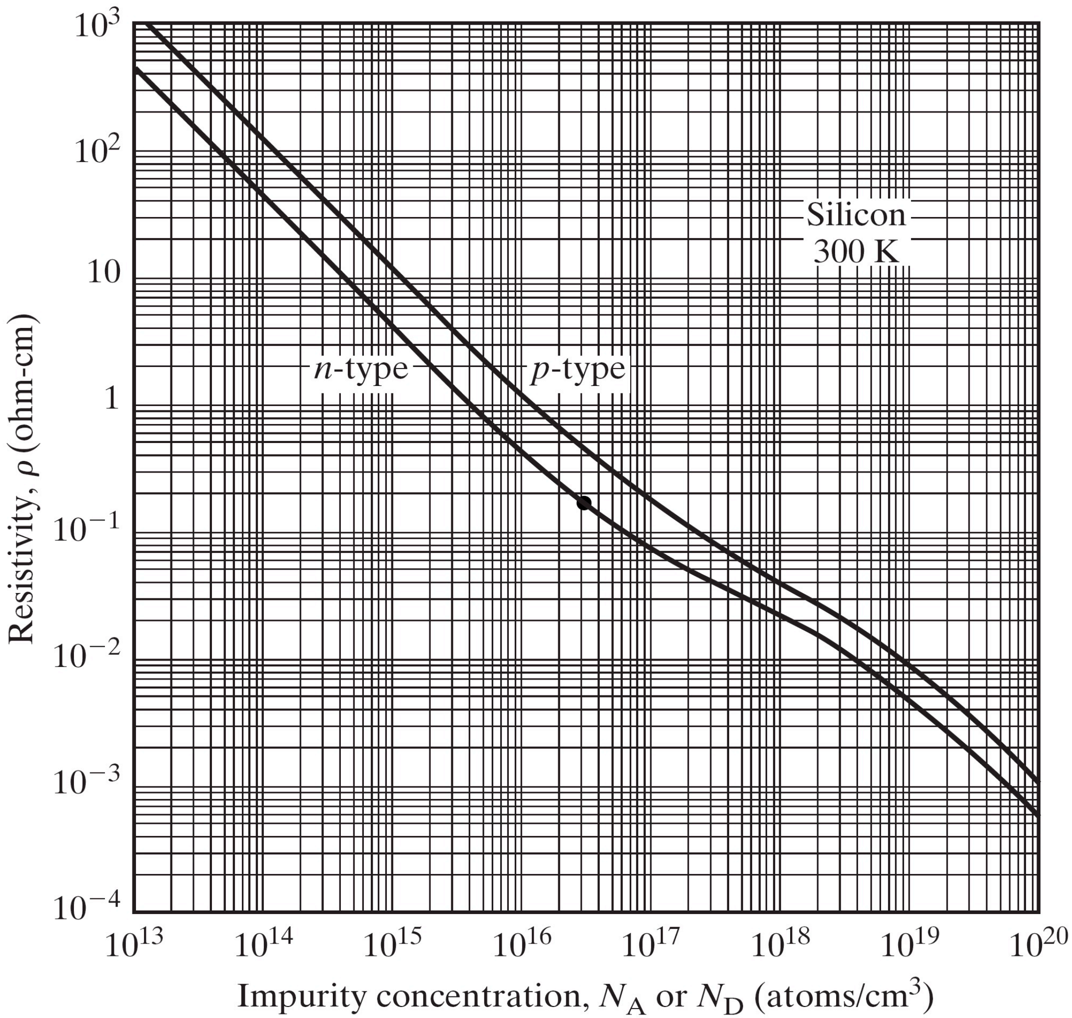


FIGURE 4.8

Room-temperature resistivity in n- and p-type silicon as a function of impurity concentration. (Note that these curves are valid for either donor or acceptor impurities but not for compensated material containing both types of impurities.) Copyright 1987 Addison-Wesley Publishing Company. Reprinted with permission from Ref. [3].

Key takeaways (Lecture #8)

- Extrinsic semiconductor (p-type):
  - Group III (such as Boron, B) atoms in silicon crystals are called acceptor impurities/atoms
  - Electrons from the valence band are excited to the acceptor level creating holes in the valence band
  - Note that in this case holes are created in the valence band without creation of electrons in the conduction band

$$p_0 = N_a + n_0$$

  - Since $p_0 > n_0$, this semiconductor is called p-type semiconductor