

# Lecture 6: Extrinsic semiconductors

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## 1 Introduction

The carrier concentration of intrinsic Si at room temperature is  $10^{10} \text{ cm}^{-3}$  and is a constant defined by the band gap of the material. This gives a conductivity of  $3 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ . To increase the conductivity one can use a lower band gap material, like Ge. But if the material cannot be changed from intrinsic Si, then the only way to increase carrier concentration is to increase temperature.

**Doping** is a method of *selectively increasing carrier concentration*, by addition of *selected impurities* to an intrinsic semiconductor. This is called an **extrinsic semiconductor**. In any semiconductor at equilibrium, the **law of mass action** should be satisfied i.e.

$$\boxed{np = n_i^2} \quad (1)$$

In an intrinsic semiconductor  $n = p = n_i$ , so equation 1 becomes trivial. But when impurities are added to a semiconductor, to increase the carrier concentration, equation 1 restricts the increase to *either* electrons or holes. Both cannot be increased simultaneously. If  $n$  increases, then  $p$  decreases,

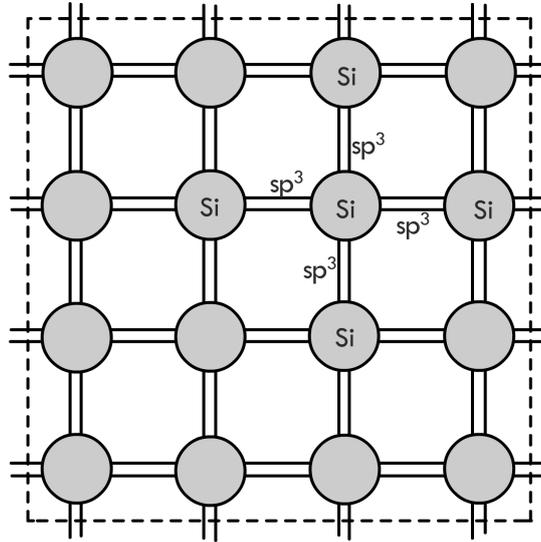


Figure 1: Two dimensional picture of Si. Each Si has 4  $sp^3$  hybrid electrons which can form a covalent bond with 4 other Si atoms. The arrangement is tetrahedral, which is shown in the figure as a two dimensional array of atoms with 4 bonds each. Adapted from *Principles of Electronic Materials - S.O. Kasap*.

and vice versa. Thus doping can selectively increase electron or hole concentration.

*An extrinsic semiconductor is formed by adding a small amount of impurities to a pure semiconductor crystal to preferentially increase carrier concentration of one polarity.* There are two important terms in this definition

1. 'small' - the concentration of impurities is very small, of the order of ppm (parts per million) or ppb (parts per billion).
2. 'impurities' - these are precisely controlled additions to a pure material. Not impurities in the sense of unwanted material. **Dopants** would be a better term for these additions.

## 2 $n$ -type doping

Consider a two dimensional picture of Si, as shown in figure 1. Si, has 4 electrons in the outer shell. The  $s$  and  $p$  orbitals hybridize to form 4  $sp^3$  orbitals. A *small* amount of *pentavalent impurity*, like As, is added to Si.

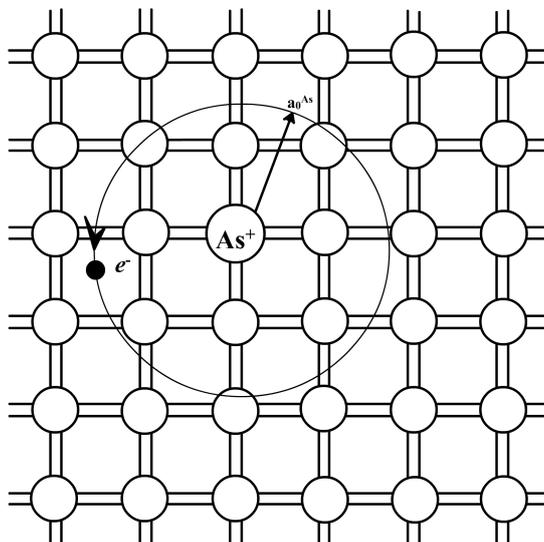


Figure 2: Si lattice with As impurity added. The As atom substitutes for Si in the lattice and *donates* one extra electron making it an *n*-type dopant. Adapted from *Principles of Electronic Materials* - *S.O. Kasap*.

The amount of impurity added is small so that the crystal structure of Si is not disturbed and the impurity behaves like individual atoms and do not form clusters. Later we will quantify the amount of As needed to increase the conductivity and show that our assumption is justified. The As atom can substitute for a Si atom in the lattice, as shown in figure 2. Since, As has 5 electrons, 4 of these are involved in bonding with the Si atom. There is an extra electron in the As atom, and if sufficient energy is supplied it can be delocalized and made available for conduction.

To calculate the energy required to delocalize the extra electron from As, a simple calculation can be done by modeling the system using a *one electron H-like atom*. The binding energy of an electron in the H atom is given by

$$E_b = -\frac{m_e e^4}{8\epsilon_0^2 h^2} = -13.6 \text{ eV} \quad (2)$$

where  $m_e$  is the mass of electron and  $\epsilon_0$  is the permittivity of free space. This equation can be modified to calculate the binding energy of the extra electron of the As atom located in the Si matrix. This can be done by using the effective mass of electron,  $m_e^*$ , and the relative permittivity ( $\epsilon_0 \epsilon_r$ ) of Si.

Equation 2 now becomes

$$E_b^{As} = E_b \frac{m_e^*}{m_e} \frac{1}{\epsilon_r^2} = -0.032 \text{ eV} \quad (3)$$

$E_b^{As}$  represents the energy required to delocalize the extra electron from As and make it available for conduction. The calculated value of 0.032 eV or 32 meV is comparable to thermal energy ( $k_B T$ ) at room temperature, which is 25 meV. Thus, when As is added to Si, there is one excess electron in the conduction band for each As atom. These electrons are available for conduction and are responsible for the large increase in conductivity by doping.

The actual value for the ionization of the electron from As, by density functional theory calculations, is around 54 meV, which is also small and comparable to thermal energy. The same argument is valid for other pentavalent impurities like P and Sb. The ionization energies for these elements are also small, P (45 meV) and Sb (39 meV), and comparable to the value for As. Pentavalent impurities like P, Sb, and As have an extra electron to ‘donate’ to the Si crystal. These impurities are called **donors**. Since the extra electron is delocalized at room temperature and are present in the conduction band the donor energy levels are located close to the conduction band. This is shown schematically in figure 3. The As atoms are localized in the Si lattice, so they are depicted as individual atomic levels in the band gap. The distance between the donor level ( $E_d$ ) and the conduction band minimum ( $E_c$ ) is the *donor ionization energy*, given by equation 3. This value is of the order of tens of meV, which is much smaller than the band gap of Si (1.10 eV). If  $N_d$  is the concentration of the donor atoms in the lattice, there are  $N_d$  extra electrons that are available for conduction. At room temperature, these electrons are located in the conduction band so that the concentration of electrons is given by  $n = N_d$ , when ( $N_d \gg n_i$ ). The concentration of holes is given by equation 1.

$$p = \frac{n_i^2}{N_d} \ll N_d \quad (4)$$

Hence the conductivity of the  $n$ -type doped Si sample is given by

$$\sigma = ne\mu_e + pe\mu_e \approx N_d e \mu_e \quad (5)$$

### 3 $p$ -type doping

Consider intrinsic Si where a trivalent impurity like B is added. The concentration of the B atoms is small so that the Si lattice is not changed by

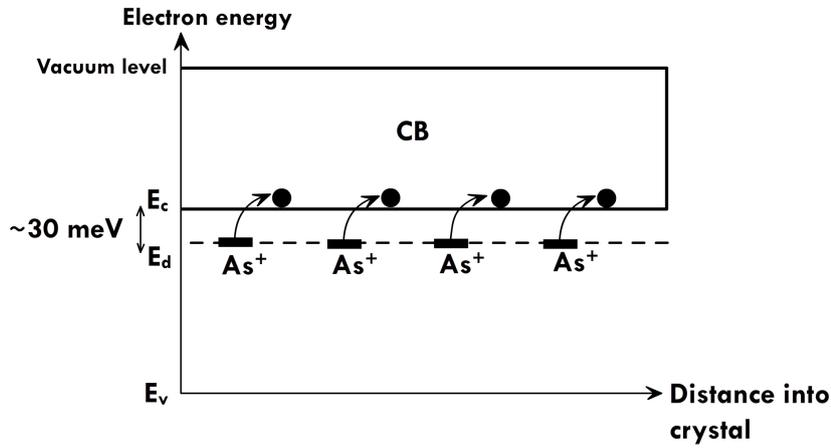


Figure 3: Si energy band with the As donor levels close to the conduction band. The As concentration is low so that its energy levels are localized. Adapted from *Principles of Electronic Materials - S.O. Kasap*.

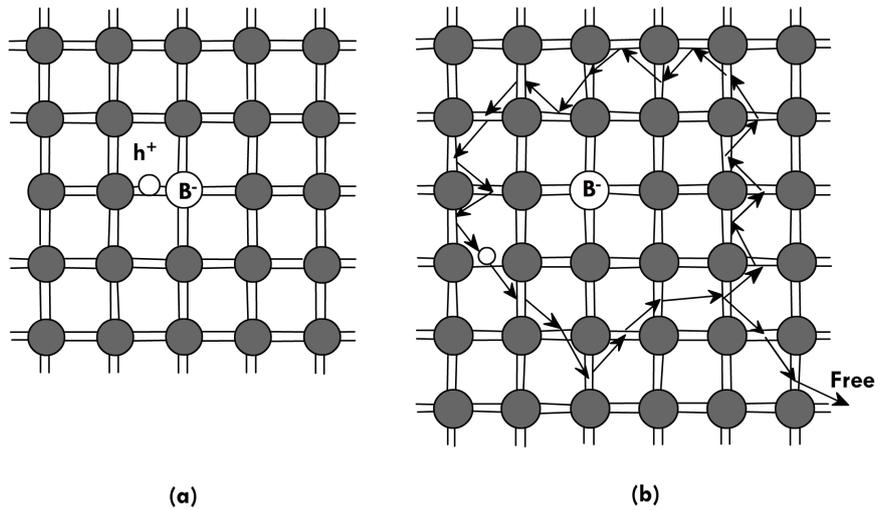


Figure 4: (a) B doping in a Si lattice. (b) The extra hole is delocalized and gets excited to the valence band. This electron is free to move in the Si lattice. Adapted from *Principles of Electronic Materials - S.O. Kasap*.

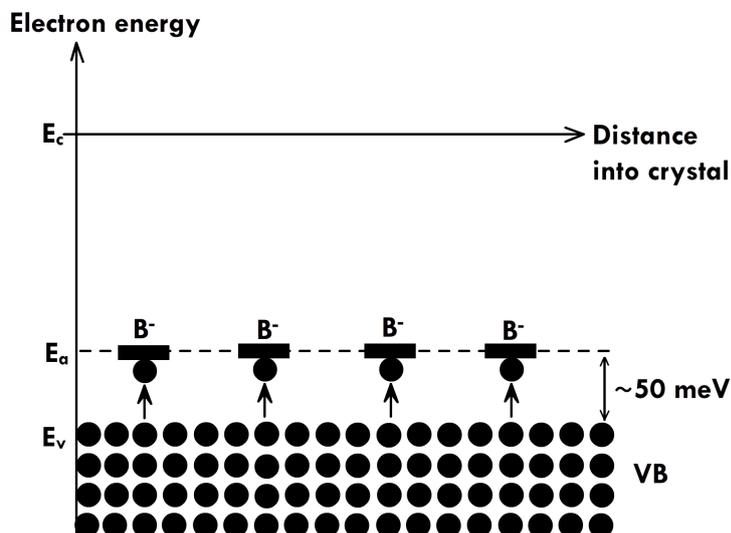


Figure 5: Acceptor energy levels are close to the valence band of the Si. Electrons from the valence band can get promoted to these levels leaving behind holes. These acceptor levels are localized due to the small concentration. Adapted from *Principles of Electronic Materials* - S.O. Kasap.

individual B atoms substitute for Si atoms in the lattice. This is shown schematically in figure 4. Since a B atom has only 3 electrons it can form 3 bonds with 3 Si atoms. But an extra electron from the valence band of Si can be excited to the B energy level to bond with the fourth Si atom. This leaves behind a hole in the valence band, that is available for conduction. The energy for ionization of the electron to the B level can be calculated in a similar manner to that for the n-type impurities. The ionization energy for various trivalent impurities like B (45 meV), Al (57 meV), and Ga (72 meV) is of the order of thermal excitation energy. So electrons from the valence band can be easily excited to the B energy level. There is one hole in the valence band for every B atom doped in the lattice. Since the trivalent atom accepts electrons from the Si, these are called **acceptors**.

Since the acceptor atoms accept electrons from the valence band their energy levels are located close to the valence band. This is shown in figure 5. The distance between the acceptor level ( $E_a$ , localized) and the valence band maximum ( $E_v$ ) is the ionization energy. If  $N_a$  is the concentration of the acceptors, then at room temperature, the concentration of holes is given

by  $p = N_a$ , when ( $N_a \gg n_i$ ). The concentration of electrons is given by equation 1.

$$n = \frac{n_i^2}{N_a} \ll N_a \quad (6)$$

Hence the conductivity of the  $p$ -type doped Si sample is given by

$$\sigma = ne\mu_e + pe\mu_e \approx N_a e \mu_h \quad (7)$$

## 4 Conductivity in extrinsic Si

Consider Si with intrinsic carrier concentration of  $10^{10} \text{ cm}^{-3}$ . It is doped with As ( $N_d$ ) of concentration  $10^{15} \text{ cm}^{-3}$ . Arsenic is an  $n$ -type dopant since it has one extra electron which is donated to the conduction band. Since each As atom donates one electron, the concentration of electrons ( $n$ ) is  $10^{15} \text{ cm}^{-3}$ , which is much larger than  $n_i$ . Concentration of holes ( $p$ ) is given by equation 1 and the value is  $10^5 \text{ cm}^{-3}$ . Thus, electrons are the **majority charge carriers** and holes are the **minority charge carriers**. The conductivity is given by equation 5 and with electron mobility ( $\mu_e$ ) of  $1350 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  the conductivity ( $\sigma$ ) is  $0.216 \text{ } \Omega^{-1}\text{cm}^{-1}$ . This is *5 orders of magnitude* higher than the conductivity of intrinsic Si.

The increase in conductivity is due to the addition of  $10^{15} \text{ cm}^{-3}$  of As. To put this number in terms of concentration, the atomic density of Si can be calculated from the density ( $2.33 \text{ g cm}^{-3}$ ) and the atomic weight ( $28 \text{ g mol}^{-1}$ ). This gives the atomic density of Si to be  $5 \times 10^{22} \text{ atoms cm}^{-3}$ . Thus, the concentration of As (that gives 5 orders of magnitude increase in conductivity) is only *20 parts per billion* of Si atoms. Thus the As ‘*impurity*’ has to be carefully controlled since it has a huge influence on the conductivity. Instead of As, if B ( $N_a$ ) is added with the same concentration of  $10^{15} \text{ cm}^{-3}$  the each B atom creates one hole, so the concentration of holes ( $p$ ) is  $10^{15} \text{ cm}^{-3}$  ( $N_a \gg n_i$ ). Electron concentration is  $10^5 \text{ cm}^{-3}$ . In a  $p$ -type semiconductor, holes are now the majority carriers and electrons the minority carriers. The conductivity is slightly lower since the hole mobility is lower but it is still orders of magnitude higher than intrinsic Si.

## 5 Compensation doping

In extrinsic doping the semiconductor is doped with either  $p$  or  $n$  type dopant. It is possible to dope both types of dopant in the same material. This type of doping is called **compensation doping**. Compensation doping is used when junctions are needed to be formed in the case of electronic devices. For

forming a  $pn$  junction, a  $n$ -doped sample is chosen and then compensated doped with  $p$ -type dopant or vice versa. If there are both donors and acceptors in a semiconductor then the one with the higher concentration will dominate so that the final material will be either  $n$  or  $p$  type. Consider a material with  $N_d$  donors and  $N_a$  acceptors. Let  $N_d$  and  $N_a$  be  $\gg n_i$ . If  $N_d > N_a$ , then the overall material is  $n$ -type with

$$\boxed{n = (N_d - N_a) \text{ and } p = \frac{n_i^2}{(N_d - N_a)}} \quad (8)$$

If  $N_a > N_d$ , then the overall material is  $p$ -type with

$$\boxed{p = (N_a - N_d) \text{ and } n = \frac{n_i^2}{(N_a - N_d)}} \quad (9)$$