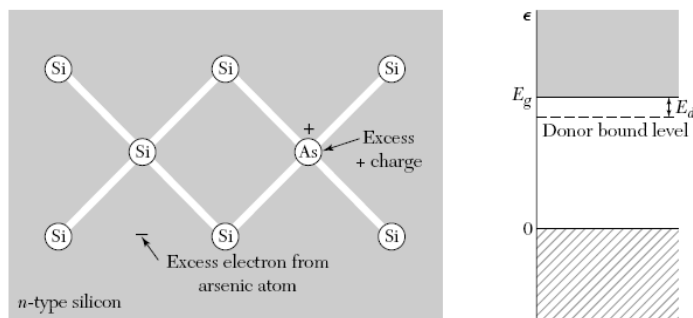


## Impurity States and their Population

A pure semiconductor has equal numbers of both types of carriers, electrons and holes. In most applications, however, one needs specimens which have one type of carrier only for example, the junction transistor. Certain impurities and imperfections drastically affect the electrical properties of a semiconductor. The addition of boron to silicon in the proportion of 1 boron atom to  $10^5$  silicon atoms increases the conductivity of pure silicon at room temperature by a factor of  $10^3$ . In a compound semiconductor a stoichiometric deficiency of one constituent will act as an impurity; such semiconductors are known as **deficit semiconductors**. The deliberate addition of impurities to a semiconductor is called **doping**. By doping the semiconductor with appropriate impurities, one can obtain samples which contain either electrons only or holes only. We consider the effect of impurities in silicon and germanium. These elements crystallize in the diamond structure. Each atom forms four covalent bonds, one with each of its nearest neighbors, corresponding to the chemical valence four. If an impurity atom of valence five, such as phosphorus, arsenic, or antimony, is substituted in the lattice in place of a normal atom, there will be one valence electron from the impurity atom left over after the four covalent bonds are established with the nearest neighbors, that is, after the impurity atom has been accommodated in the structure with as little disturbance as possible. Impurity atoms that can give up an electron are called **donors**.

**Donor States:** The structure in Fig. 1 has a positive charge on the impurity atom (which has lost one electron). Lattice constant studies have verified that the pentavalent impurities enter the lattice by substitution for normal atoms, and not in interstitial positions. The crystal as a whole remains neutral because the electron remains in the crystal. The extra electron moves in the coulomb potential  $e/\epsilon r$  of the impurity ion, where  $\epsilon$  in a covalent crystal is the static dielectric constant of the medium.



We estimate the ionization energy of the donor impurity. The Bohr theory of the hydrogen atom may be modified to take into account the dielectric constant of the medium and the effective mass of an electron in the periodic potential of the crystal. The ionization energy of atomic hydrogen is  $-e^4 m / 2\hbar^2$

In the semiconductor with dielectric constant  $\epsilon$  we replace  $e^2$  by  $e^2/\epsilon$  and  $m$  by the effective mass  $m_e$  to obtain

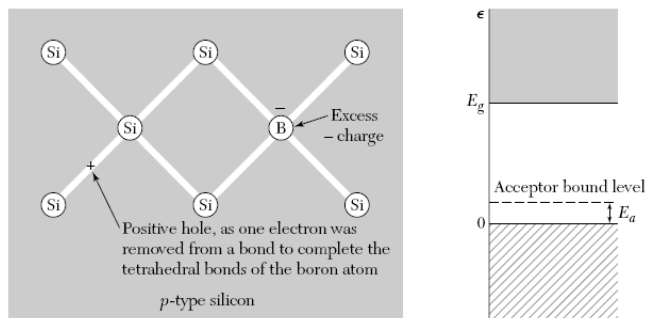
$$E_d = \frac{e^4 m_e}{2\epsilon^2 \hbar^2} = \left( \frac{13.6 m_e}{\epsilon^2 m} \right) eV$$

Using the Bohr radius of the ground state of the Bohr radius of the donor is

$$a_d = \frac{\epsilon \hbar^2}{m_e e^2} = \left( \frac{0.53 \epsilon}{m_e/m} \right) \text{\AA}$$

The semiconductor can conduct in the impurity band by electrons hopping from donor to donor. The process of impurity band conduction sets in at lower donor concentration levels if there are also some acceptor atoms present, so that some of the donors are always ionized. It is easier for a donor electron to hop to an ionized (unoccupied) donor than to an occupied donor atom, in order that two electrons will not have to occupy the same site during charge transport.

**Acceptor States:** A hole may be bound to a trivalent impurity in germanium or silicon Fig. 2, just as an electron is bound to a pentavalent impurity. Trivalent impurities such as B, Al, Ga, and In are called **acceptors** because they accept electrons from the valence band in order to complete the covalent bonds with neighbor atoms, leaving holes in the band.



When an acceptor is ionized a hole is freed, which requires an input of energy. On the usual energy band diagram, an electron rises when it gains energy, whereas a hole sinks in gaining energy. The Bohr model applies qualitatively for holes just as for electrons, but the degeneracy at the top of the valence band complicates the effective mass problem. The donor and acceptor

ionization energies in Si are comparable with  $k_B T$  at room temperature (26 meV), so that the thermal ionization of donors and acceptors is important in the electrical conductivity of silicon at room temperature. If donor atoms are present in considerably greater numbers than acceptors, the thermal ionization of donors will release electrons into the conduction band. The conductivity of the specimen then will be controlled by electrons (negative charges), and the material is said to be  $n$  type. If acceptors are dominant, holes will be released into the valence band and the conductivity will be controlled by holes (positive charges): the material is  $p$  type.

#### Concentration of Impurity States

Semiconductors usually contain both donors and acceptors. Electrons in the CB can be created either by interband thermal excitation or by thermal ionization of the donors. Holes in the VB may be generated by interband excitation, or by thermal excitation of electrons from the VB into the acceptor level. And in addition, electrons may fall from the donor levels to the acceptor level. Finding the concentrations of carriers-both electrons and holes-under the most general of circumstances, taking all these processes into account, is quite complicated. Instead of giving the details of such general calculations here, we shall treat a few special cases instead, ones which are often encountered in practice. Two regions may be distinguished, depending on the physical parameters involved: The intrinsic and the extrinsic regions.

#### The intrinsic region

The concentration of carriers in the intrinsic region is determined primarily by thermally induced interband transitions. Consequently we have, to a good approximation;

$$n = p$$

In that case, we find the carrier concentrations as given in previous lecture;

$$n_i = p_i = 2 \left( \frac{k_B T}{2\pi\hbar^2} \right)^{3/2} (m_e m_h)^{3/4} \exp(-E_g/2k_B T)$$

This is known as the intrinsic concentration, denoted by  $n_i$ . The intrinsic region obtains when the impurity doping is small. When we denote the concentrations of donors and acceptors by  $N_d$ , and  $N_a$ , the requirement for the validity of the intrinsic condition is

$$n_i \gg (N_d - N_a)$$

Suggesting there are  $N_d$ , electrons at the donor level, but of these a number  $N_a$  may fall into the acceptors, leaving only  $N_d - N_a$  electrons to be excited from the donor level into the conduction band.

When above condition is satisfied, the ionization of all these remaining impurities is not sufficient to appreciably affect the number of electrons excited thermally from the VB. The semiconductor may then be treated as a pure sample, and the influence of impurities disregarded. Since  $n_i$ , increases rapidly with temperature, the intrinsic condition becomes more favorable at higher temperatures. All semiconductors, in fact, become intrinsic at sufficiently high temperatures (unless the doping is unusually high).

### **The extrinsic region**

Quite often the intrinsic condition is not satisfied. For the common dopings encountered, about  $10^{15} \text{ cm}^{-3}$ , the number of carriers supplied by the impurities is large enough to change the intrinsic concentration appreciably at room temperature. The contribution of impurities, in fact, frequently exceeds those carriers that are supplied by interband excitation. When this is so, the sample is in the extrinsic region.

Two different types of extrinsic regions may be distinguished. The first occurs when the donor concentration greatly exceeds the acceptor concentration, that is, when  $N_d \gg N_a$ . In this case, the concentration of electrons may be evaluated quite readily. Since the donor's ionization energy is quite small, all the donors are essentially ionized, their electrons going into the CB. Therefore, to a good approximation;

$$n = N_d$$

The hole concentration is small under this condition. To calculate this concentration, we make the following useful observation. For intrinsic semiconductor we have found

$$np = 4 \left( \frac{k_B T}{2\pi\hbar^2} \right)^3 (m_c m_h)^{3/2} \exp(-E_g/k_B T)$$

This relation is valid whether the sample is pure or doped. Thus the product  $np$  is independent of  $E_F$ , and hence of the amount and type of doping; the product  $np$  depends only on the temperature. For intrinsic semiconductor we may write

$$np = n_i^2$$

This equation means that, if there is no change in temperature, the product  $np$  is a constant, independent of the doping. If the electron concentration is increased, by varying the doping, the

hole concentration decreases, and vice versa' When the doping is primarily of the donor type,  $n = N_d$ , the concentration of holes is

$$p = \frac{n_i^2}{N_d}$$

Since we are in the extrinsic region,  $n_i \ll N_d$  and hence  $p \ll N_d = n$ . Thus the concentration of electrons is much larger than that of holes. A semiconductor in which  $n \gg p$  is called an n-type semiconductor. The other type of extrinsic region occurs when  $N_a \gg N_d$ , that is, the doping is primarily by acceptors. Using an argument similar to the above, one then has

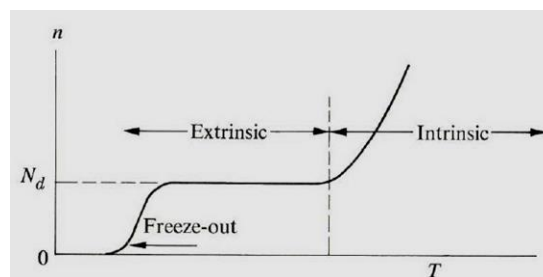
$$p \sim N_a$$

i.e., all the acceptors are ionized. The electron concentration, which is small, is given by

$$n = \frac{n_i^2}{N_a}$$

Such a material is called a p-type semiconductor. It is characterized by a preponderance of holes (acceptors).

In discussing ionization of donors (and acceptors), we assumed that the temperature is sufficiently high so that all of these are ionized. This is certainly true at room temperature. But if the temperature is progressively lowered, a point is reached at which the thermal energy becomes too small to cause electron excitation. In that case, the electrons fall from the CB into the donor level, and the conductivity of the sample diminishes dramatically. This is referred to as freezeout, in that the electrons are now "frozen" at their impurity sites.



The variation of the electron concentration with temperature in an n-type sample is indicated schematically in which the various regions freeze-out, extrinsic, intrinsic-are clearly marked.