Eq. 12.17 may be used to determine E_g of a semiconductor. If we take the natural log of Eq. 12.17, we obtain

$$\ln n = \ln n_0 - \frac{E_g}{2kT} \qquad (12.18)$$

Therefore, if we measure the current I through a semiconductor as a function of T at constant voltage, as in Fig. 12.1, then Eq. 12.18 implies that ln I will be a linear function of $\frac{1}{T}$ with slope $-\frac{E_g}{2k}$.

12.5.4 Extrinsic Semiconductors: Doping

As we have seen, intrinsic semiconductors are inherently rather poor conductors. By themselves, they would not be very useful. The power of semiconductor materials comes mostly from the fact that by adding small amounts of the right kind of impurity, one can greatly increase the concentration of charge carriers. Furthermore, this can be done in two different, independent ways, so that either the concentration of free electrons or the concentration of free holes is greatly enhanced. In other words, one can modify a semiconductor so that electrical current is carried only by electrons, or only by holes.

To introduce these types of impurities is referred to as **doping** the pure material. The impurities themselves are called **dopants**. The method is general and works with all kinds of pure (i.e. undoped) semiconductors, but for a given material, only a handful of elements are suitable as dopants. I will explain the principle by focusing on the most important material, namely Si.

> The *principle of doping*:
>
> In order for an impurity to be able to act as a dopant (in a manner to be described), the impurity atoms must have one valence electron more or less than the atoms they replace. This means that for Si, being a Group IVA material in the periodic table, the dopants must be either from Group IIIA or Group VA.

How doping works is best explained with a picture, Fig. 12.12. Our example is *Si with P as the dopant*.

The P atoms, being from Group VA, have five valence electrons. When a P atom replaces a Si atom, only 4 of the 5 valence electrons make covalent bonds with the Si neighbors. The 5th electron is bound only very loosely to the P atom and is easily removed. Once it has moved away from its atom of origin, it is free !

The crucial thing in this case is that no strong Si-Si bonds need to be broken in order to create free electrons from the dopants. The energy required for shaking loose the 5th electron on the P atom is much smaller than the Si-Si
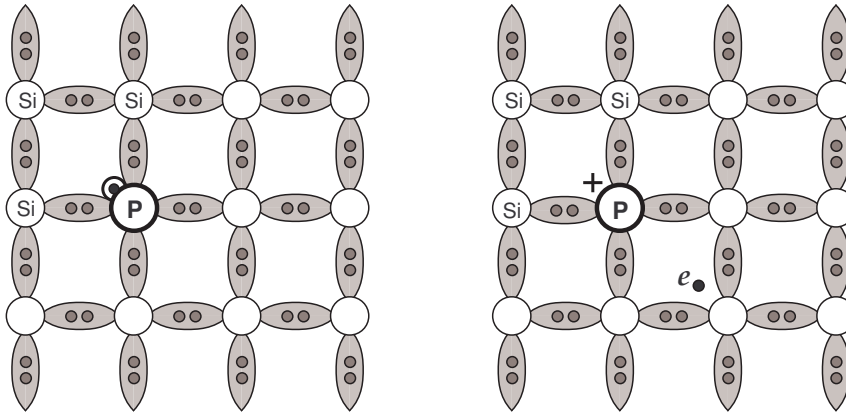
Figure 12.12: Si doped with P. Left panel: The 5th valence electron is still on the P atom. Right panel: The electron has been detached from P and made free.

bond energy. At the same time, please note that as an electron is freed from a P atom, ***no hole is created*** ! The positive charge left behind by the freed electron remains on the P atom, in effect making it an immobile P^+ ion. Hence, this type of doping preferentially enhances the concentration of free electrons.

Doping with a Group VA dopant makes the Si a so-called **n-type semiconductor**. The n in n-type refers to the extra negative charge carriers, i.e. the additional free electrons provided by the dopants. An n-type dopant is also called a **donor**, since it donates an electron to the conduction band.

In semiconductors it is often true that what applies to electrons also applies, in a slightly modified fashion, to holes. So it is with doping. Again let us consider an example, ***Si with B as the dopant***, a Group IIIA atom.

On the left in Fig. 12.13, the B atom is shown in its normal, neutral state. It has only three valence electrons and thus can make covalent bonds to only 3 of its 4 Si neighbors. However, it takes only very little net energy to remove an electron from a Si-Si bond and use it to complete the fourth B-Si bond. The broken Si-Si bond is the same as in Fig. 12.11, a hole free to move around the Si crystal.

This type of doping with a Group III dopant makes the Si a so-called **p-type semiconductor**. The p in p-type refers to the extra positive charge carriers, i.e. the additional free holes created by the dopants. A p-type dopant is also called an **acceptor**, since it takes on an electron from the valence band. Note that for each positive hole created, a negative charge remains on the B atom, in effect making it an immobile B^- ion.

Now we are in a position to connect our discussion of doping, breaking and reforming electron bonds, back to the picture of energy bands and electron energy states. In fact, some people argue that energy bands, and how they are
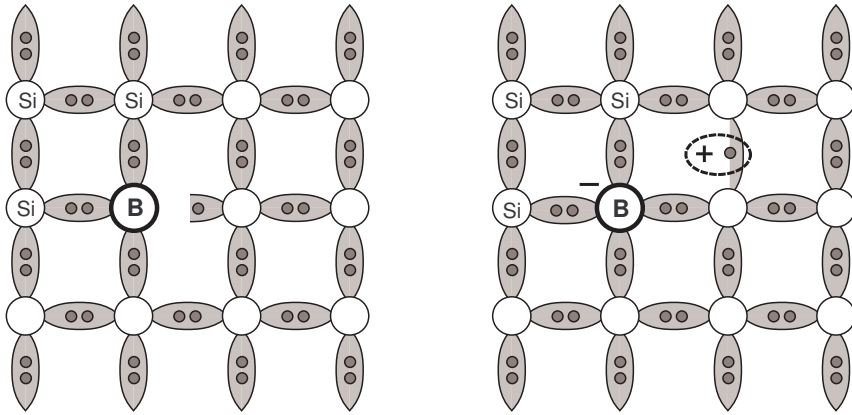
Figure 12.13: Si doped with B. Left: B atom with covalent bonds to three Si neighbors. Right: An electron from a Si-Si bond is used to make the fourth B-Si bond, and create a free hole.

populated by electrons, are the more fundamental description. However, both bonds and bands provide useful, but different, perspectives on the ultimate physical reality.

On the basis of what we know about what happens in doping, we can construct corresponding energy diagrams as follows:
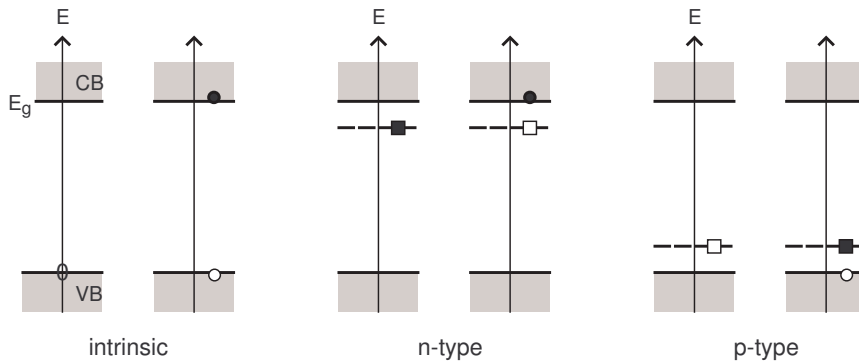

Figure 12.14: Energy band structures of intrinsic, n-type, and p-type semiconductors. The two graphs in each panel illustrate the non-excited state, and the state with free charge carriers either in the CB (n-type), or in the VB (p-type), or in both bands (intrinsic).

You will recognize that these bands are basically the same as those for the semiconductors in Fig. 12.5. The minor difference is that the bandgap region is magnified, and only the band edges are shown, not the entire bands. The zero

of the energy scale is arbitrary. It is set conveniently at the top of the VB. This puts the bottom of the CB at $E = E_g$.

Free charge carriers are indicated by circles: electrons in the CB, and holes in the VB. The dashed lines denote extra energy states introduced by the dopants, let us say again either P or B. For n-type material, the fifth electron on P is held only loosely and excited easily to the CB. But as long as this electron is on the P, it is in an energy level just a little below the bottom of the CB. For p-type material, an initially empty energy level on B is located just a little above the top of the VB, but can easily be populated by an electron from the VB.

The squares denote immobile states. The open square in the middle panel stands for a P atom which has given off an electron to the CB. The filled square in the right panel stands for a B atom which has taken on an electron from the VB.

The point of doping a semiconductor material is really threefold:

1. Doping allows one to *increase the conductivity of the base semiconductor material* by many orders of magnitude.
   We saw in the discussion of intrinsic material, that around room temperature the intrinsic concentration of electrons n_i is typically of the order of $10^{16}m^{-3}$ in Si. However, the purest Si material people can produce contains impurities at a level of about $10^{19}m^{-3}$. This is still incredibly pure compared to other engineering materials. But it means that intrinsic Si is not a real world material. It is used mostly as a hypothetical standard of comparison.
   Practical levels of doping range from about $10^{20}m^{-3}$ to $10^{25}m^{-3}$. They are often limited by how soluble a dopant is in Si.

2. By introducing dopants, one can *engineer the conductivity of the semi-conducting material* quite precisely.
   Under normal conditions and with typical doping levels, it is the charge carriers created by the dopants that dominate the material's conducting properties. The intrinsic concentrations are much smaller than the concentrations caused by doping. Therefore, intrinsic concentrations are practically negligible.

3. The two types of dopants enable the materials engineer to create two types of conductors, with either negative or positive charge carriers, i.e. with free electrons or free holes. It is this option that makes it possible to *construct all sorts of electronic devices*, by combining the two types of materials in clever ways, as we shall below.

The conductivity σ is much simpler to determine for a doped material. The reason is that the majority charge carrier, i.e. the one due to the dopant, is present in much higher concentration that the other carrier. Moreover, for Si at around room temperature, to a very good approximation all dopants are ionized. Thus the two types of doping work out as follows: