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Chapter

2

SEMICONDUCTORS AND *P-N* JUNCTIONS

2.1 SEMICONDUCTORS

In 1839 Becquerel observed that certain materials, when exposed to light, produced an electric current (Becquerel, 1839). This is now known as the photovoltaic effect, and is the basis of the operation of photovoltaic or solar cells.

Solar cells are manufactured from semiconductor materials; that is, materials that act as insulators at low temperatures, but as conductors when energy or heat is available. At present, most solar cells are silicon-based, since this is the most mature technology. However, other materials are under active investigation and may supersede silicon in the long term.

The electrical properties of semiconductors can be explained using two models, the *bond* and the *band* models. These models are described briefly below. (More detailed descriptions are given in Green, 1992 and Neville, 1978.)

2.1.1 The bond model

The bond model uses the covalent bonds joining the silicon atoms to describe semiconductor behaviour. Fig. 2.1 illustrates the bonding and the movement of electrons in a silicon crystal lattice.



Figure 2.1. Schematic representation of covalent bonds in a silicon crystal lattice.

At low temperatures, the bonds are intact and the silicon behaves as an insulator. At high temperatures, some bonds are broken and conduction can occur by two processes:

- 1. Electrons from broken bonds are free to move.
- 2. Electrons from neighbouring bonds can also move into the 'hole' created in the broken bond, allowing the broken bond or hole to propagate as if it had a positive charge.

The concept of a moving hole is analogous to that of a bubble in a liquid. Although it is actually the liquid that moves, it is easier to describe the motion of the bubble going in the opposite direction.

2.1.2 The band model

The band model describes semiconductor behaviour in terms of the energy levels between valence and conduction bands. This is illustrated in Fig. 2.2.



Figure 2.2. Schematic of the energy bands for electrons in a solid.

The electrons in covalent bonds have energies corresponding to those in the *valence band*. In the *conduction band* the electrons are free. The *forbidden gap* corresponds to the minimum energy needed to release an electron from a covalent bond to the conducting band where it can conduct a current. The *holes* remaining conduct in the opposite direction in the valence band, as described for the bond model.

2.1.3 Doping

It is possible to shift the balance of electrons and holes in a silicon crystal lattice by 'doping' it with other atoms. Atoms with one more valence electron than the semiconductor are used to produce '*n*-type' material. Atoms with one less valence electron result in '*p*-type' material. This is illustrated in Fig. 2.3.



Figure 2.3. Schematic of a silicon crystal lattice doped with impurities to produce *n*-type and *p*-type semiconductor material.

2.2 SEMICONDUCTOR TYPES

Silicon and other semiconductor materials used for solar cells can be crystalline, multicrystalline, polycrystalline, microcrystalline or amorphous. Although usages of these terms vary, we follow the definitions by planar grain size according to Basore (1994). Microcrystalline material has grains smaller than 1 μ m, polycrystalline smaller than 1 mm and multicrystalline smaller than 10 cm. The structure of the different material types is illustrated in Fig. 2.4.



Figure 2.4. The structure of crystalline, multicrystalline and amorphous silicon.

2.2.1 Crystalline silicon

Crystalline silicon has an ordered crystal structure, with each atom ideally lying in a pre-ordained position. It therefore allows ready application of the theories and techniques developed for crystalline material, described in previous sections, and exhibits predictable and uniform behaviour. It is, however, the most expensive type of silicon, because of the careful and slow manufacturing processes required. The cheaper multicrystalline or polycrystalline silicon (poly-silicon), and amorphous silicon are therefore increasingly being used for solar cells, despite their less ideal qualities.

2.2.2 Multicrystalline silicon

The techniques for production of multicystalline or polycrystalline silicon are less critical, and hence cheaper, than those required for single crystal material. The grain boundaries reduce the cell performance by blocking carrier flows, allowing extra energy levels in the forbidden gap, thereby providing effective recombination sites, and providing shunting paths for current flow across the p-n junction.

To avoid significant recombination losses at grain boundaries, grain sizes in the order of a few millimetres are required (Card & Yang, 1977). This also allows single grains to extend from the front to the back of a cell, providing less resistance to carrier flow and generally decreasing the length of grain boundaries per unit of cell. Such multicrystalline material is widely used for commercial solar cell production.

2.2.3 Amorphous silicon

Amorphous silicon can be produced, in principle, even more cheaply than polysilicon. With amorphous silicon, there is no long-range order in the structural arrangement of the atoms, resulting in areas within the material containing unsatisfied, or 'dangling' bonds. These in turn result in extra energy levels within the forbidden gap, making it impossible to dope the semiconductor when pure, or to obtain reasonable current flows in a solar cell configuration.

It has been found that the incorporation of atomic hydrogen in amorphous silicon, to a level of 5–10%, saturates the dangling bonds and improves the quality of the material. It also increases the bandgap (E_g) from 1.1 eV in crystalline silicon to 1.7 eV, making the material much more strongly absorbing for photons of energy above the latter threshold. The thickness of material required to form a functioning solar cell is therefore much smaller.

The minority carrier diffusion lengths in such silicon-hydrogen alloys, (a-Si:H), are much less than 1 μ m. The depletion region therefore forms most of the active carrier-collecting volume of the cell. Different design approaches to those discussed above for crystalline silicon are therefore used. In particular, as large a 'depletion region' as possible is created. Fig. 2.5 illustrates the general design of an a-Si:H solar cell.



Figure 2.5. Schematic of an a-Si:H solar cell.

Amorphous silicon and other 'thin film' technologies for solar cell manufacture, where films of very thin semiconductor material are deposited onto glass or other substrates, are used in many small consumer products, such as calculators and watches, 'non-critical' outdoor applications and, increasingly also for large scale applications. In principle, thin films provide a very low cost means of cell production, although at present their efficiencies and lifetimes are lower than for crystalline products. Research into thin film and other potentially low cost solar cell materials may see these technologies dominate the solar cell market over coming decades.

2.2.4 Thin film crystalline silicon

A very wide range of methods are being investigated to develop thin film silicon cells deposited on foreign substrates (Green, 2003). If the ratio of hydrogen to silane in the gas from which amorphous silicon is deposited is increased, the resulting material becomes microcrystalline, with columns of crystallites separated by amorphous regions. The optical and electronic properties are similar to those of bulk silicon. Such material has been used as an alternative to silicon-germanium alloys in hybrid structures with amorphous silicon. Particular measures are necessary to allow the amorphous layers to be kept thin enough to avoid light-induced degradation while producing similar current to the microcrystalline cell(s) in series. A microcrystalline/ amorphous tandem design has been developed with an efficiency of about 11% on a laboratory scale.

One company is approaching commercial production with a process in which a thin film silicon cell is formed on a textured glass superstrate. A laser is used to form craters through the active material to contact the *n*-type layer closest to the glass. Low quality material is deposited, then improved by subsequent thermal steps.

2.3 ABSORPTION OF LIGHT

When light falls onto semiconductor material, photons with energy (E_{ph}) less than the bandgap energy (E_g) interact only weakly with the semiconductor, passing through it as if it were transparent. However, photons with energy greater than the bandgap energy $(E_{ph} > E_g)$ interact with electrons in covalent bonds, using up their energy to break bonds and create *electron-hole pairs*, which can then wander off independently. This is illustrated in Fig. 2.6.



Figure 2.6. The creation of electron-hole pairs when illuminated with light of energy $E_{\rho h}$ = *h*f, where $E_{\rho h}$ > E_{g} .

Higher energy photons are absorbed closer to the surface of the semiconductor than lower energy photons, as illustrated in Fig. 2.7.



Figure 2.7. The light energy dependency of electron-hole generation.

The generation rate (G) of electron-hole (e-h) pairs per unit volume can be calculated using the formula:

$$G = \alpha N e^{-\alpha x} \tag{2.1}$$

where N is the photon flux (photons per unit area per second), α is the absorption coefficient, and x is the distance from the surface. The value of α as a function of the wavelength of light is illustrated in Fig. 2.8 for silicon at 300 K.



Figure 2.8. The absorption coefficient, α , of silicon at 300 K as a function of the vacuum wavelength of light.

2.4 RECOMBINATION

When the light is switched off, the system must return to a state of equilibrium and the electron-hole pairs generated by the light must disappear. With no external source of energy, the electrons and holes wander around until they meet up and *recombine*.

Any defects or impurities within or at the surface of the semiconductor promote recombination.

The *carrier lifetime* of a material is defined as the average time for recombination to occur after electron-hole generation. For silicon, this is typically 1 μ s. Similarly, the *carrier diffusion length* is the average distance a carrier can move from point of generation until it recombines. For silicon, this is typically 100–300 μ m. These two parameters give an indication of material quality and suitability for solar cell use. However, no power can be produced from a semiconductor without a means of giving directionality to the moving electrons. Therefore, functional solar cells are typically produced from semiconductor material by the addition of a rectifying *p*-*n* junction.

2.5 P-N JUNCTIONS

A *p*-*n* junction is formed by joining *n*-type and *p*-type semiconductor materials, as shown in Fig. 2.9.



Figure 2.9. Formation of a *p-n* junction.

When joined, the excess holes in the *p*-type material flow by diffusion to the *n*-type material, while electrons flow by diffusion from the *n*-type material to the *p*-type material as a result of the carrier concentration gradients across the junction. The electrons and holes leave behind exposed charges on dopant atom sites, fixed in the crystal lattice. An electric field (\hat{E}) therefore builds up in the so-called *depletion region* around the junction to stop the flow. Depending on the materials used, a 'built-in' potential (V_{bi}) owing to \hat{E} will be formed. If a voltage is applied to the junction, as shown in Fig. 2.10, \hat{E} will be reduced.



Figure 2.10. Application of a voltage to a *p*-*n* junction.

Once \hat{E} is no longer large enough to stop the flow of electrons and holes, a current is produced. The built in potential reduces to $V_{bi} - V$ and the current flow increases exponentially with the applied voltage. This phenomenon results in the *Ideal Diode Law*, expressed as

$$I = I_0 \left[\exp\left(\frac{qV}{kT}\right) - 1 \right]$$
(2.2)

where I is the current, I_0 is the dark saturation current (the diode leakage current density in the absence of light), V is the applied voltage, q is the charge on an electron, k is Boltzmann's constant and T is absolute temperature.

Note that

- I_0 increases as T increases
- I_0 decreases as material quality increases
- at 300 K, kT/q = 25.85 mV, the *thermal voltage*.

For actual diodes, the Eqn. (2.2) becomes

$$I = I_0 \left[\exp\left(\frac{qV}{nkT}\right) - 1 \right]$$
(2.3)

where n is the ideality factor, a number between 1 and 2 that typically increases as the current decreases.

The diode law is illustrated for silicon in Fig. 2.11.



Figure 2.11. The diode law for silicon—current as a function of voltage for temperatures T_1 and T_2 ($T_2 > T_1$). For a given current, the curve shifts by approximately 2 mV/°C.

EXERCISES

- 2.1. The absorption coefficient of silicon decreases from 1.65×10^6 cm⁻¹ at 0.3 µm wavelength, to 4400 cm⁻¹ at 0.6 µm and 3.5 cm⁻¹ at 1.1 µm. Assuming zero reflection from both front and rear surfaces at each wavelength, calculate and sketch the generation rate of electron-hole pairs, normalised to the surface generation rate, across a silicon cell of 300 µm thickness.
- 2.2. In terms of the electronic properties of semiconductors, explain why the absorption coefficient increases with increasing photon energy, for energies near the semiconductor bandgap (see Green, 1992 or similar for further information).

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