Even though the behavior of $CuInSe_2$ provides a good basis for the understanding of device-quality material, there are pronounced differences when Ga and Na are present in the films. More recently, $Cu(InGa)Se_2$ has been reviewed in the context of solar cells with an emphasis on electronic properties [27].

In this section the structural, optical, and electrical properties of $CuInSe_2$ are reviewed along with information about the surface and grain boundaries and the effect of the substrate. In each case, as appropriate, the effect of the alloying with $CuGaSe_2$ to form $Cu(InGa)Se_2$ and the impact of Na and O on the material properties will be discussed.

13.2.1 Structure and Composition

$CuInSe_2$ and $CuGaSe_2$ have the chalcopyrite lattice structure. This is a diamond-like structure similar to the sphalerite structure but with an ordered substitution of the group I (Cu) and group III (In or Ga) elements on the group II (Zn) sites of sphalerite. This gives a tetragonal unit cell depicted in Figure 13.3 with a ratio of the tetragonal lattice parameters c/a close to 2 (see Table 13.1). The deviation from $c/a = 2$ is called the tetragonal distortion and stems from different strengths of the Cu–Se and the In–Se or Ga–Se bonds.

The possible phases in the Cu–In–Se system are indicated in the ternary phase diagram in Figure 13.4. Thin films of Cu–In–Se prepared under an excess supply of Se, that is, normal conditions for thin-film growth of $Cu(InGa)Se_2$, have compositions that fall on, or close to, the tie-line between Cu_2Se and In_2Se_3. Chalcopyrite $CuInSe_2$ is located on this line as well as a number of phases called ordered defect compounds (ODC), because they have a lattice structure described by the chalcopyrite structure with an ordered insertion of intrinsic defects. A comprehensive study of the Cu–In–Se phase diagram has been completed by Gödecke *et al.* [32]. A detail of the Cu_2Se–In_2Se_3 tie-line near $CuInSe_2$ is described by the pseudobinary phase diagram reproduced in Figure 13.5 [32] Here α is the chalcopyrite $CuInSe_2$, δ is a high-temperature (HT) phase with the sphalerite structure, and β is an ODC phase. It is interesting to note that the single phase field for $CuInSe_2$ at low temperatures is relatively narrow as compared to earlier beliefs, and does not contain

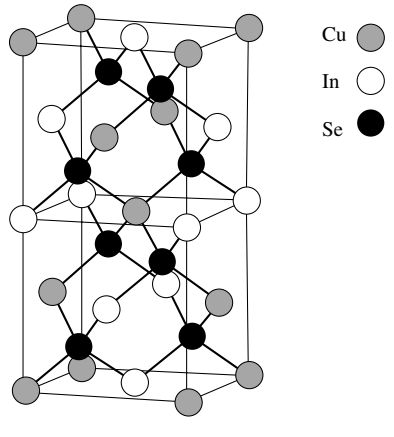

Figure 13.3 The unit cell of the chalcopyrite lattice structure