Kesterites

Figure 13.1 shows the abundance in the Earth's crust for several elements. As we can see, indium is a very rare element. However, it is a crucial element of CIGS solar cells. Because of its scarcity, In might be *the* limiting step in the upscaling of the CIGS PV technology to future terawatt scales. In addition, the current thin-film display industry depends on In as well, as ITO is integrated in many display screens.

As a consequence, other chalcogenic semiconductors are investigated that do not contain rare elements. A interesting class of materials are the *kesterites* which are *quarternary* or *pentary* semiconductors consisting of four or five elements, respectively. While the name giving mineral kesterite [$Cu_2(ZnFe)SnS_4$], where zinc and iron atoms can substitute each other, is not used as a semiconductor, kesterite without iron (Cu_2ZnSnS_4) is used. It also is known as *copper zinc tin sulphide* (CZTS) and is a I_2-II-IV-VI_4 semiconductor. Other kesterites are for example *copper zinc tin selenide* ($Cu_2ZnSnSe_4$, CZTSe), or ones using a mixture of sulphur and selenium, $Cu_2ZnSn(SSe)_4$ (CZTSS).

In difference to CIGS, CZTS is based on non-toxic and abundantly available elements. The current record efficiency is 12%. It is achieved with an CZTSS solar cells on lab-scale by IBM [47].

13.4.2 Cadmium telluride solar cells

In this section we will discuss the *cadmium telluride* (CdTe) technology, which currently is the thin-film technology with the lowest demonstrated cost per W_p. We start with discussing the physical properties of CdTe, which is a II-VI semiconductor because it consists of the II valence electron element cadmium (Cd) and the VI valence electron element tellurium (Te). Like the III-V semiconductors discussed in Section 13.2, CdTe forms a *zincblende* lattice structure where every Cd atom is bonded to four Te atoms and vice versa.

The bandgap of CdTe is 1.44 eV, a value which is close to the optimal bandgap for single junction solar cell. CdTe is a direct bandgap material, consequently only a few micrometres of CdTe are required to absorb all the photons with an energy higher than the bandgap energy. If the light-excited charge carriers should be efficiently collected at the contacts, their diffusion coefficient has to be in the order of the thickness.

CdTe can be *n*-doped by replacing the II-valence electron atom Cd with a III-valence electron atom like aluminium, gallium or indium. *n*-doping can be achieved as well by replacing a VI-valence tellurium atom with a VII-valence electron element like fluorine, chlorine, bromine and iodine atoms. The III- and VII-valence atoms act as shallow donors. Also a tellurium vacancy acts like a donor.

p-doping of CdTe can be achieved by replacing Cd with a I-valence electron atom like copper, silver or gold. It can be achieved as well by replacing Te atoms with V-valence electron elements such as nitrogen, phosphorus or arsenic. These elements act as shallow acceptors. But also a Cd vacancy acts as an acceptor. In solar cells, *p*-doped CdTe is used. However, it is difficult to obtain CdTe with a high doping level.

Figure 13.22 (a) shows the structure of a typical CdTe solar cell. First, transparent front contact is deposited onto the glass superstrate. This can be *tin oxide* or *cadmium stannate*, which is a Cd-Sn-oxide alloy. On top of that the *n*-layer is deposited, which is a *cadmium sulphide* layer, similar to the *n*-buffer layer in CIGS solar cells (Section 13.4.1). Then, the *p*-type CdTe absorber layer is deposited with a typical thickness of a few micrometers.
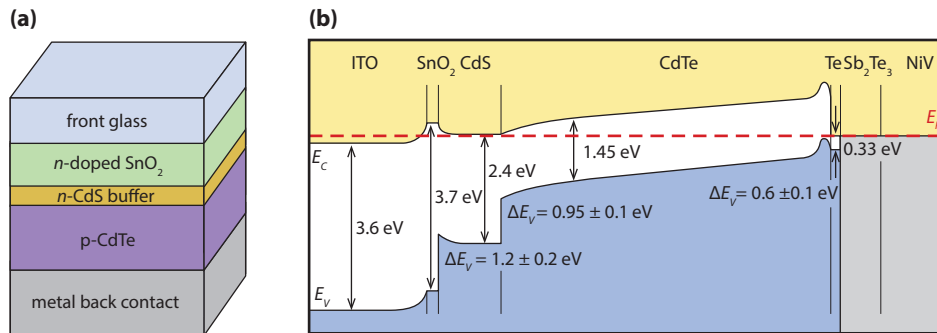
(a)   **(b)**

Figure 13.22: The (a) layer structure and (b) band diagram of a typical CIGS solar cell. Band diagram data taken from [83].

Making a good back contact on CdTe is rather challenging because the material properties of CdTe restrict the choice of acceptable metals. Heavily doping the contact area with a semiconductor material improves the contact qualities; however, achieving high doping levels in CdTe is problematic. Copper containing contacts have been used as back contacts, however, on the long term they may face instability problems due to diffusion of Cu through the CdTe layer up to the CdS buffer layer. Nowadays, stable *antimony telluride* layers in combination with molybdenum are used.

The band diagram of a CdTe solar cell is shown on Fig. 13.22 (b). The *p*-type semiconductor CdTe has a bandgap of 1.44 eV whereas the *n*-type CdS has a bandgap of 2.4 eV. Consequently, the junction is a heterojunction, similar to what we have seen for CIGS PV devices. The light excited minority electrons in the *p*-layer are separated at the heterojunction and collected at the TCO based front contact. The holes are collected at the back contact.

Manufacturing CdTe solar cells

Usually, the CdS/CdTe layers are processed using the *closed-space sublimation method*. In this method, the source and the substrate are placed at a short distance from each other, ranging from a few millimetres up to several cm, under vacuum conditions.The source can either consist of granulates or powders of CdTe. Both, the source and the substrate are heated, where the source is kept at a higher temperature than the substrate. This temperature difference induces a driven force on the precursors, which are deposited on the substrate. Such, the bulk *p*-type CdTe is formed. In the process chamber, an inert carrier gas like argon or nitrogen can be used.

The US company First Solar Inc. is the leading company in the CdTe technology [84]. Like the German company Antec Solar, they use the closed space sublimation method. Another company producing CdTe solar cells is the German Calyxo. First Solar is by far the largest CdTe manufacturer. In 2008, First Solar had an annual production rate of 500 MW. In 2006 and 2007 it already was one of the biggest solar module manufacturers in the world.

The record conversion efficiency of lab-scale solar CdTe solar cells is 19.6% [47] and was

obtained by GE Global Research in 2013. The open circuit voltage of this cell is 857.3 mV, the short circuit current density is 28.59 mA/cm^2, and the FF is 80.0%. The current record module based on CdTe technology has a conversion efficiency of 16.1% at an area of 7200 cm^2.

The current cost of modules from First Solar product is in the order of 0.68 to 0.70 USD/W$_p$ and is expected to drop to 0.40 USD/W$_p$, hence keeping the cost per W$_p$ lower than that of modules based on crystalline silicon wafers.

An important aspect that needs to be addressed is the toxicity of cadmium. However, insoluble Cd compounds like CdTe and CdS are much less toxic than the elementary Cd. Nonetheless, it is very important to prevent cadmium entering into the ecosystem. It is an important question whether, CdTe modules could become a major source of Cd pollution. As of 2014, First Solar has an installed *nameplate capacity* of 1.8 GW$_p$/year.[85] With this capacity, about 2% of the total industrial Cd consumption would be taken by First Solar. Nevertheless, recycling schemes have been set up for installed CdTe solar modules. For example, First Solar has a recycling scheme in which a deposit of 5 dollar cents per W$_p$ is included to cover the cost for the recycling at the end of the module lifetime.

Maybe an even bigger challenge for the CdTe technology is the supply with tellurium. Let us take another look at Fig. 13.1 that shows the abundance of the various elements in the Earth's crust. Tellurium is one of the rarest stable solid elements in the Earth's crust with an abundance of about 1 µg/kg, which is comparable to that of platinum [86]. Because of its scarcity, the supply with Te might be the limiting step to upscale the CdTe PV technology to future terawatt scales. On the other hand, Tellurium as source material has only had a few users so far. Thus, for Te no dedicated mining has been explored so far. In addition, new supplies of tellurium-rich ores were found in Xinju, China. In conclusion, at this moment it remains unclear to which extent the CdTe PV technology might be limited by the supply with tellurium.

13.5 Organic photovoltaics

So far we discussed inorganic thin-film semiconductor materials such as III-V semiconductors, amorphous and nanocrystalline silicon, CIGS and CdTe solar cells. In this section we will take a look at *organic photovoltaics*. The used absorber materials are either *conductive organic polymers* or *organic molecules* that are based on carbon, which may form a cyclic, a-cyclic, linear or mixed compound structure.

Figure 13.23 shows some example of organic materials that can be used for PV applications: P3HT, Phtalocyanine, PCBM and Ruthenium Dye N3. All these materials can be considered as large conjugated systems, which means that carbon atoms in the chain have an alternating single or a double bond and every atom in the chain has a p-orbital available. In such conjugated compounds, the p-orbitals are delocalised, which means that they can form one big mixed orbital. Hence, the valence electron of the original p-orbital is shared over all the orbitals. A classical example would be the benzene molecule, which is a cyclic conjugated compound. As we can see in Fig. 13.24 (a), This molecule has 6 carbon atoms and six p-orbitals, which mix and from two circular orbitals that contain three electrons each. These electrons do not belong to one single atom but to a group of atoms.

In contrast, a methane molecule (CH$_4$) is tetrahedrally coordinated, which means that it