

pure CuInSe<sub>2</sub> absorbers [14]. With evaporation it is difficult to nucleate and grow very thin continuous CdS layers such as those normally used in current state-of-the-art Cu(InGa)Se<sub>2</sub> devices, and the optical transmission of the window will be limited to energies less than the CdS band gap, 2.4 eV. Substrate temperatures of 150 to 200°C are used to obtain good optical and electrical properties of the evaporated CdS films. This is substantially higher than the substrate temperature used for chemical bath deposition. Improved device performance was achieved by alloying the evaporated CdS with ZnS [15]. Mixed (CdZn)S has a wider band gap, allowing increased optical transmission, and better lattice match to Cu(InGa)Se<sub>2</sub> than CdS.

The main drawback with vacuum evaporation is poor conformal coating resulting in nonuniform and incomplete coverage of the sometimes relatively rough Cu(InGa)Se<sub>2</sub> films. Sputter deposition leads to more conformal coverage. The general success of sputtering for industrial large-area deposition motivated the exploration of sputter-deposited CdS buffer layers. Using optical emission spectroscopy to control the sputtering process, Cu(InGa)Se<sub>2</sub> devices with efficiencies up to 12.1% were fabricated, as compared to 12.9% for reference cells with chemical bath-deposited CdS [137]. Both evaporation and sputtering are vacuum processes, which can be incorporated in-line with other vacuum processing steps and do not create any liquid wastes. Still, CBD remains the preferred process for the CdS layer owing to its advantages in forming thin conformal coatings.

Atomic layer chemical vapor deposition (ALCVD) is a method that also allows accurate control of the growth of thin conformal layers [138]. The method is being industrially used for deposition of another II-VI compound, ZnS. Inorganic precursors for deposition of CdS require the substrate temperature to be excessively high (>300°C) and work with organic precursors has been limited. The strong driving force for replacement of the environmentally nondesirable cadmium has focused the development of ALCVD on materials other than CdS. This is also valid for regular CVD, although some metal organic CVD (MOCVD) work has been reported. The full potential for chemical vapor-deposited CdS has therefore not been explored.

Electrodeposition can be used to deposit CdS films but its use has not been reported in Cu(InGa)Se<sub>2</sub> devices.

#### 13.4.4 Alternative Buffer Layers

The cadmium content in Cu(InGa)Se<sub>2</sub> PV modules with CBD CdS buffer layers is low. Investigations show that the cadmium in Cu(InGa)Se<sub>2</sub> modules can be handled safely, both with respect to environmental concerns and hazards during manufacturing (see Section 13.6.5). In spite of this, it would be preferable to eliminate cadmium in new products. There are in principle two approaches to Cd-free devices: (1) finding a buffer material that replaces CdS and (2) omitting the CdS layer and depositing ZnO directly onto the Cu(InGa)Se<sub>2</sub> film. In practice, the two approaches tend to merge when the chemical bath deposition of CdS is replaced with a surface treatment of the Cu(InGa)Se<sub>2</sub> with no or negligible film deposition before the subsequent deposition of the ZnO.

A number of approaches and materials have been tried. A selection of promising results are presented in Table 13.3.